STUDIES ON THE NUTRIENT CHEMISTRY OF CHALIYAR RIVER ESTUARY

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CERTIFICATE

This is to certify that this thesis bound herewith is an authentic record of the research carried out by Shri. Jose K. Xavier, M.Sc., under my supervision and guidance in the National Institute of Oceanography, Regional Centre, Cochin, in partial fulfillment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part thereof has been previously formed the basis of the award of any degree, diploma or associateship in any University.

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PREFACE

India has several major estuarine systems scattered all along the east and west coasts. Due to the differences in the physico-chemical, biological and meteorological conditions that exist in different regions of our country, generalisation becomes somewhat difficult, necessitating detailed study on each estuary.

Chaliyar river estuary is one of the major estuarine systems in the south-west coast of India. Study on the nutrient chemistry of this estuary was lacking and nutrient flux studies has not been reported from any of the Indian estuaries. In the present work, an attempt has been made to study systematically the general hydrography, nutrient chemistry and fluxes of inorganic nutrients.

The present thesis, "Studies on the nutrient chemistry of Chaliyar river estuary" is based on the intensive sampling and analysis of nutrient data and other environmental parameters collected at 8 stations covering 4 sections in the Chaliyar river estuary. Two hourly synoptic sampling was done at all stations covering one tidal cycle, once in a month for a period of one year (October 1990 to September 1991). The results and discussions are presented in six chapters.

Chapter 1 gives a general introduction about estuaries and describes the importance of the study of nutrients in estuaries along with the scope of the present investigation. Chapter 2 describes the study area with station locations.

The sampling procedure and analytical methods employed together with a brief account of the data presentation techniques adopted are also discussed in this chapter.

In chapter 3 the distribution and seasonal variation of different hydrographic parameters such as temperature, salinity, pH and dissolved oxygen in the estuary are discussed. Chapter 4 presents the results on the distribution and spatio-temporal variations of different nitrogen and phosphorus fractions in the estuary. Tidal variations are analysed to investigate the extent to which tides affected these parameters. Inter-relationship between various parameters are analysed using statistical methods and is discussed in this chapter.

Chapter 5 deals with nutrient flux studies and discusses the net fluxes and transport of nutrients through various cross-sections in the Chaliyar river estuary. Chapter 6 summarises the salient features of the investigation followed by a list of references.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

An estuary is the place where river meets an inlet of the sea. Pritchard (1967) defined an estuary as a "semi-enclosed coastal body of water which has a free connection with open sea and within which sea water is measurably diluted with fresh water derived from land drainage". Fairbridge (1980), in his review on the definitions of estuaries argues that the tidally affected freshwater region should be considered an integral part of any estuary. The estuaries grouped under these definitions have a salinity significantly lower than the open sea and are termed positive estuaries. Negative estuaries are those where evaporation exceeds river flow plus precipitation and hypersaline condition exists.

Estuaries are divided into three geomorphologically defined categories: the fjord type, the barbuilt type and the coastal plain estuary. Fjords are generally deep with a relatively large body of semi-enclosed seawater below a brackish surface layer. Bar built estuaries are generally associated with depositional coasts and have characteristic bars across their mouths. The coastal plain estuary is a submerged extension of a river valley opening towards the sea.

The majority of estuaries that have been studied fall within the coastal plain category and within this group large differences occur in the circulation patterns, density stratification and mixing processes. The chemistry of estuaries should be considered in the context of the physical processes of water circulation which occur in them, since the distribution of dissolved and particulate substances are controlled by the circulation and mixing of their waters (Aston, 1978). Consequently, a better classification would be the one based on the salinity distribution and flow characteristics within the estuary. It is the interaction between processes arising from river discharge on one hand and the tidal currents on the other, which leads to the occurrence of a series of types of estuary circulation, described in detail by Dyer (1973), Officer (1976) and Bowden (1980). At one extreme is the salt wedge type estuary, in which the influence of river discharge is dominant and freshwater flows out of the estuary as a surface layer above an intruding wedge of seawater. At the other extreme, when the tidal currents are dominant, the water is almost completely mixed vertically and there is little variation in salinity with depth. The partially mixed type estuary is an intermediate case in which there is a gradual increase of salinity from surface to bottom, with a net seaward flow in the upper layer and an upstream flow below it.

1.1. Estuarine Chemical Reactivity

Estuarine ecological environments are complex and highly variable compared to other marine environments. The dominant feature controlling the distribution, speciation and reactivity of chemical components within estuaries is the mixing of fresh and saline waters. Differences in the nature of the fresh and saline mixing components produce gradients and transitions of physico-chemical properties within an estuary in response to the circulation and mixing pattern. Estuaries are characterised by complex gradients of salinity, tidal action, current velocity, bottom erosion and sediment accumulation. They are subject to major and often unpredictable variations in response to river flow as well as wind and storm patterns.

In an estuary, mixing occurs between natural waters of very different chemical composition and physico-chemical properties. Although the salinity of sea water is high as compared with the total salt content of river waters, the plant nutrient elements nitrogen, phosphorus and silicon are higher in fresh water than in seawater. Ionic strength and physico chemical parameters such as pH and redox potential may change during estuarine mixing. Estuarine waters also contain suspended solids derived from the inflowing river or seawater or by resuspension of settled sediment as a result of tidal stirring.

Characterization of estuarine samples with respect to salinity is a standard procedure for chemical investigations in estuaries and is known as the 'reactant method' (Morris,1985). Correlation of the concentration of a dissolved chemical species with salinity for samples collected throughout the salinity range allows an assessment of gain, loss or conservation of the constituent and an indication of the relative contributions of the species from the separate marine and freshwater sources. One can also deduce the salinity related location of reactivity and the extent to which it has progressed.

1.2. Study of nutrients in estuaries

The term 'nutrients' usually refers to the dissolved inorganic forms of nitrogen, phosphorus and silicon utilised by photosynthetic organisms in the formation of organic matter. Nitrogen and phosphorus are described as being biolimiting elements, which means that the concentration of these elements limits biological growth. The processes that govern the fate of these elements in estuaries differ and consequently the ratios of inorganic nitrogen to phosphorus in estuaries may vary widely with time and space.

Estuaries are generally regarded as one of the most productive of aquatic systems and the nutrient supply from freshwater inputs is important in sustaining their high rates of primary production. Estuaries function as important sinks and transformers of nutrients, thus altering the quantity and quality of nutrients transported from land to the sea (Jordan et al., 1991).

On an areal basis of any class of ecosystems, esturies receive some of the highest inputs of nutrients because of the local influences from land drainage and often pollution.

A number of estuaries receive nutrient additions (per unit area) over 1000 times the fertilizer loads added to agricultural areas (Nixon et al., 1986). The resulting nitrogen and phosphorus inputs lead to elevated phytoplankton productivity (Ryther and Dunston, 1971; Nixon and Pilson, 1983; Keller, 1988) and can lead to hypoxia and eutrophication. There has been an increase in recent years in the rates of eutrophication of lakes, rivers and estuaries due to the release of nitrates and phosphates from excess fertilisers and sewage effluents (O'Neill, 1985). The great concern over this problem has stimulated much new research in the following areas: the chemistry and biogeochemistry of nutrients in aquatic systems, the quantification of the sources and sinks of nutrients, and the dynamics of nutrient uptake and release.

The distribution and variation of nutrients in estuarine systems are controlled by a variety of physical, geological, chemical and biological processes (Pritchard and Schubel,1981). Understanding the behaviour of nutrients in estuaries has important implications for global nutrient budgets and for controlling eutrophication of these systems. The study on the hydrographical features and the effect of nutrient enrichment is essential in understanding the water as a useful resource. A discussion of the sources and sinks of nutrients and their distribution with the estuarine system is of great importance. Perhaps one of the most pivotal questions concerning nutrients in estuaries is the degree to which estuaries behave as traps, retaining and recycling nutrients within the system and the relative contributions of external nutrient supply.

A successful understanding of the role of estuaries as nutrient traps, filters or exporters requires a knowledge of the distribution of dissolved and particulate nutrient species as well as their rates of input, loss, and accumulation in coastal waters. The nutrient budget or mass balance can be a useful tool in describing the fate of nutrients in estuaries. While point source inputs from rivers and sewage treatment plants have been successfully quantified for a number of systems (Loder and Glibert, 1980; Jaworski, 1981; Smith, 1981; Nixon and Pilson, 1983; Childers and Day,1988), the more spatially variable or sporadic inputs from groundwater seepage, surface runoff, precipitation, and offshore waters are much more difficult to measure. The potentially largest term in most estuarine nutrient budgets is the exchange of nutrients with offshore waters, which is usually determined by difference or ignored due to difficulties involved in measuring small nutrient exchange differences in relatively larger tidal volumes (Kjerfve et al., 1982). In addition, nutrient accumulation rates in estuarine sediments are difficult to measure against the large background of C, N, or P already present, and are complicated by resuspension, bioturbation, and deposition rates that vary widely over time and location (Nowicki and Oviatt, 1990).

The interaction between sediments and overlying water has been recognised as an important factor in the nutrient dynamics of estuarine and marine systems. Highly metabolizable material from autogenic and exogenic sources may be deposited on to the sediment. The subsequent processes that take place at the sediment-water interface are of a complex nature and involve microbial breakdown reactions and adsorption/desorption equilibria between the liquid and solid phase. Due to these diagenetic processes, the interstitial water of the sediment is generally enriched in various nutrients as compared to the overlying water. This concentration difference will lead to an effective transport of nutrients back into the overlying water through diffusion and other mixing processes.

1.3. The Chaliyar River Estuary

The Chaliyar river is one of the major west flowing rivers of the Kerala State. It originates from the Western Ghats and joins the Arabian Sea at Beypore, near Kozhikode in the south-west coast of India. The Chaliyar river estuary is a typical positive estuary. Earlier, a few studies have been conducted in this estuary on salinity intrusion (James and Sreedharan, 1983), and on circulation and mixing (James and Ramanathan, 1983). Distribution of nutrients in the Beypore estuary have been reported by Sarala Devi et al.(1983) and their study was confined to the river mouth only. Premchand et al.(1987) have examined the circulation and flushing characteristics of this estuary during south-west monsoon season. The salinity distribution pattern and its relationship with dissolved oxygen has been studied by Giridhar Hadnooker et al. (1987). Nirmala et al. (1990) have studied the effect of salinity variation along with other hydrographical parameters on the ecology of this estuary.

Earlier wokers were using the name 'Beypore estuary' because most of the studies were confined to the river mouth which is situated at Beypore. The present study area covers 15Km upstream of Chaliyar from the river mouth and will be referred here 'Chaliyar river estuary'.

1.4. Scope Of The Present Work

The present work was undertaken with the main objective of studying the nutrient chemistry of the estuary and to make a sincere attempt in estimating nutrient fluxes. The studies were mainly directed at identifying the sources and sinks of nutrients and defining the important geochemical and biochemical pathways of nutrients in the estuary. The quantity of nutrient salts introduced by the fresh water flow into the estuary is considerable. What happens to the large quantities of nutrients that enter the estuary is not only of ecological interest but also is relevant to water quality management.

Together with other hydrographical parameters, the distribution and seasonal variation of nutrients in the estuary was studied in detail. Large temporal variations of nutrient concentrations have been shown to occur within a tidal period at fixed locations. Hence more attention was given to determine the temporal as well as spatial variations of constituents in the estuary.

India has several major estuarine systems distributed all along the east and west coasts. Extensive studies on the hydrographical, biological and physico-chemical aspects of these aquatic systems have been made by many workers. So far no attempt has been made to study the nutrient fluxes in any of the Indian estuaries. In the present work, an attempt has been made to study the fluxes of inorganic nutrients through various cross-sections in the Chaliyar river estuary. The results were analysed to determine the relative influences of riverine and tidal forcing on the fluxes.

CHAPTER 2

MATERIALS AND METHODS

2. MATERIALS AND METHODS

2.1. Description of the study area

The Chaliyar is the third largest river of Kerala state. It originates from the Ilambaliri hills in Gudalur Taluk of Nilgiri district in TamilNadu at an elevation of 2066m above mean sea level (Anonymous, 1974). Chaliyar flows towards the west from the Western Ghats and joins the Arabian Sea at Beypore near Kozhikode (Calicut). The river has a length of 169Km and the total drainage area is about 2923 Km^2 out of which $2535Km^2$ lie in Kerala state and the remaining $388Km^2$ in Tamil Nadu. The Chaliyar river estuary has a port handling cargo and a fishery harbour at Beypore situated at 11° 08'N latitude and 75° 51'E longitude.

The Chaliyar river estuary enters the sea in a south westerly direction and this inlet is situated in a stable region. There is a horse-shoe shaped bar at the entrance and the depths over it vary from 1.5m to 1.9m. The sea bed slope at Beypore is comparatively flat with a 9m contour at a distance of 3.5 Km from the river mouth. The predominant wave heights off the Beypore coast during monsoon and fair weather seasons are 1.2m and 0.6m respectively. The tides at Beypore are of mixed semi-diurnal type with a period of 12 hrs and 40 minutes (Anonymous, 1969).

Maximum river discharge occur during the south-west monsoon months June to August, and during this period, the tidal limit comes down to a distance of 5 Km from the river mouth. The lowest discharges are found to occur during April-May, and during this period tidal incursion of sea water was observed upto a distance of about 28 Km from the river mouth (James and Sreedharan, 1983). Bottom sediments in the estuary composed of silty sands in shallow areas and clayey silts in deeper areas. Towards upstream of the river, the bottom is mainly sandy with a small percentage of silt.

2.2. Station location

A map of the area of study with location of stations is given in Fig 2.1. Eight stations along four transects across the estuary were occupied. Section 1 is near to the river mouth and the upstream sections are at distances of 5, 10 and 15 Km respectively from the mouth. The two stations selected at each transect were almost equi-distant from the shore, one each on the northern and southern side. Depths along these sections varied with the tide and season, so that mean values and exceptions are stated below.

The physical dimensions of the sections are:
Section 1 (S-1) - Width = 390m; mean depth = 2.45m to 2.95m.
Section 2 (S-2) - Width = 294m; mean depth = 2.99m to 3.50m.
A pocket of deeper water with a mean depth of $\simeq$7m occupies the northern side which is localised. Midway and further south along the axis the mean depth is <3m.
Section 3 (S-3) - Width = 200m; mean depth = 4.0m to 4.54m.
Section 4 (S-4) - Width = 243m; mean depth = 2.52m to 3.06m.

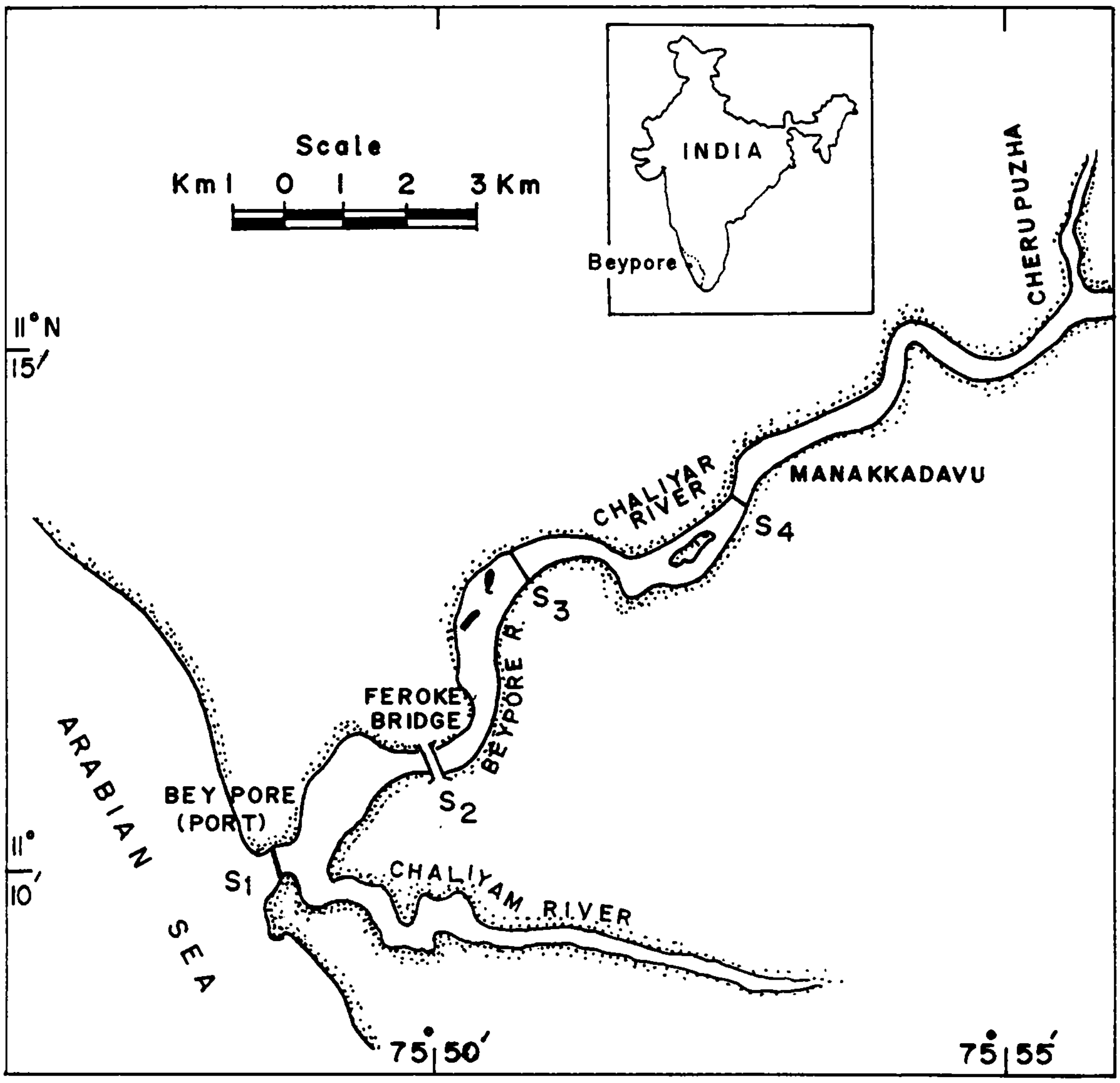


Fig. 2.1. Observation sections in Chaliyar river estuary.

2.3. Sampling procedure

Monthly surveys were conducted in the estuary for a period of one year from October 1990 to September 1991. 13 - hour tidal observations were made simultaneously at two sections on two consecutive days to get a synoptic picture. Two stations were covered across each section during these surveys. Hourly observations were made for physical parameters such as temperature, salinity and current speed and direction. Current speed and direction measurements were made using an indigenous rotor current meter (accuracy for velocity ±1 cm/sec and direction ±2.68°, designed by NIO,Goa).

Water samples were collected at two hourly intervals from the surface, mid-depth and near bottom of the water column. Surface samples were collected using a clean plastic bucket and Niskin sampler was used for collection of mid and near bottom samples. Sampling was done with the tide and in the least possible time to minimise errors. Samples for dissolved oxygen determination were collected in 125 ml stoppered glass bottles, taking care that no air bubbles are getting trapped in the sample. These samples were fixed immediately with manganous chloride solution (Winkler A) followed by alkaline potassium iodide (Winkler B) solution. Water samples for the analysis of salinity and nutrients were collected in pre-cleaned polythene bottles. Temperature and pH of the water samples were measured in situ and the samples for nutrient analyses were transported to the laboratory keeping them in ice boxes. Analysis of ammonia-N, nitrite-N, nitrate-N and inorganic phosphate were conducted immediately at the temporary laboratory set up near the observation site. Other chemical parameters such as salinity, urea-N, total N and total P were measured after bringing the samples to the permanant laboratory.

Sediment samples were collected from all stations at the time of high and low water using a hand operated Van Veen grab. Always the undisturbed middle portion of the grab sample was transferred to wide-mouth polythene bottles using a plastic spatula and kept air tight in ice-boxes for the analysis of interstitial water. The same sediment samples were used for the determination of grain size, nitrogen and phosphorus content.

2.4. ANALYTICAL METHODS

2.4.1. pH, Salinity and Dissolved Oxygen

pH measurements were made using a portable pH meter (PHILIPS, model PP 9046, accuracy ±0.01) and salinity was measured with an electrodeless induction type salinometer (DIGI-AUTO, model 3G, Tsurumi Seiki, Japan, accuracy $\pm 0.01 \times 10^{-3}$) after proper calibration.

Dissolved oxygen was determined by the Winkler's method, in the form reccommended by Strickland and Parsons(1972). The principle of the determination and the possible sources of systematic errors are fully discussed by Grasshoff(1983).

2.4.2. Nutrients

(a)Ammonia-N was determined according to the indophenol blue method of Koroleff[1] (1983). In a moderately alkaline medium, ammonia reacts with hypochlorite to form monochloramine which in the presence of phenol,catalytic amount of nitroprusside ions and excess hypochlorite forms indophenol blue. The formation of monochloramine requires a pH between 8 and 11.5. At higher pH, ammonia is incompletely oxidised to nitrite. Both calcium and magnesium ions in sea water precipitate as hydroxide and carbonate at pH higher than 9.6, however their precipitation can be prevented by complexing them with citrate buffer.

Great care was taken to ensure that samples,blanks and standards are not contaminated during the course of analysis. The samples were 'fixed' by the addition of reagents immediately after collection and the absorbance, after the colour developement (about 6 hours) was measured at 630 nm. The measured ammonia include both free dissolved ammonia gas and the ammonium ions.

(b)Nitrite was measured by the method of Bendschneider and Robinson (1952). In this method, nitrite in the water sample when treated with sulphanilamide in acid solution results in a diazo compound which reacts with N-1-naphthyl ethylene diamine dihydrochloride to form an azo dye. The absorbance of it is measured at 543 nm.

(c)Nitrate-N in the water sample was quantitatively reduced to nitrite by passing through a reduction column filled with copper coated cadmium granules and measured as nitrite. During the reduction stage, ammonium chloride buffer was added to the sample to maintain a stable pH (Grasshoff et al., 1983). The estuarine samples containing high concentration of nitrate-N were properly diluted before passing through the column.

(d)Urea-N was determined by the diacetyl monoxime method as described by Koroleff[2] (1983). In strongly acidic solutions and in the presence of a weak oxidant, urea forms a condensation product with diacetyl monoxime. This product interacts with semicarbazide and manganous ions to produce a magenta molecular complex, the absorbance of which is measured at 520 nm. Chloride ions are added in excess to increase the sensitivity of the reaction and the presence of phosphate ions enables reasonable reproducibility.

(e)Total N and P were determined by the simultaneous oxidation procedure (Koroleff[3], 1983). In this method, the water samples were oxidised with the help of a strong oxidising agent such as alkaline persulphate by autoclaving in closed condition. The organic forms of nitrogen and phosphorus and their inorganic forms in lower oxidation states are finally oxidised to nitrate and inorganic phosphate respectively. After cooling, these digested samples were estimated by the previously discussed standard procedures for nitrate and phosphate.

The calibration curve for total-N obtained with standard EDTA solutions is shown in Fig.2.4. For 1cm cell, the calibration factor obtained was 22.5. The percentage recovery of total-N using the above method was estimated with glycine standards within the concentration range of 10 to 50 ugat/l. The results are summarised in Table 2.4.1.

(f)Phosphate: Determination of inorganic phosphate involves the measurement of the concentration of orthophosphate ions by the formation of a reduced phosphomolybdenum blue complex in an acid solution containing molybdic acid, ascorbic acid and trivalent antimony. The most popular of the methods relying on this reaction, which was developed by Murphy and Riley (1962) is that given by Strickland and Parsons (1972). A variation of this method described by Grasshoff et al. (1983) is adopted in the present work. Instead of single solution reagent as in the Murphy and Riley procedure, two stable reagent solutions are used here. 0.5 ml of the mixed reagent containing molybdic acid and antimony tartrate followed by 0.5 ml of ascorbic acid reagent were added to 25 ml aliquots of the samples. The absorbance was measured in 5cm cuvettes at 882 nm within 30 minutes to reduce any possible interference from arsenate. Turbidity corrections were made wherever found necessary.

2.4.3. Interstitial Water

Interstitial water was extracted from wet sediment samples using the Reeburg's squeezer (Reeburg, 1967). The

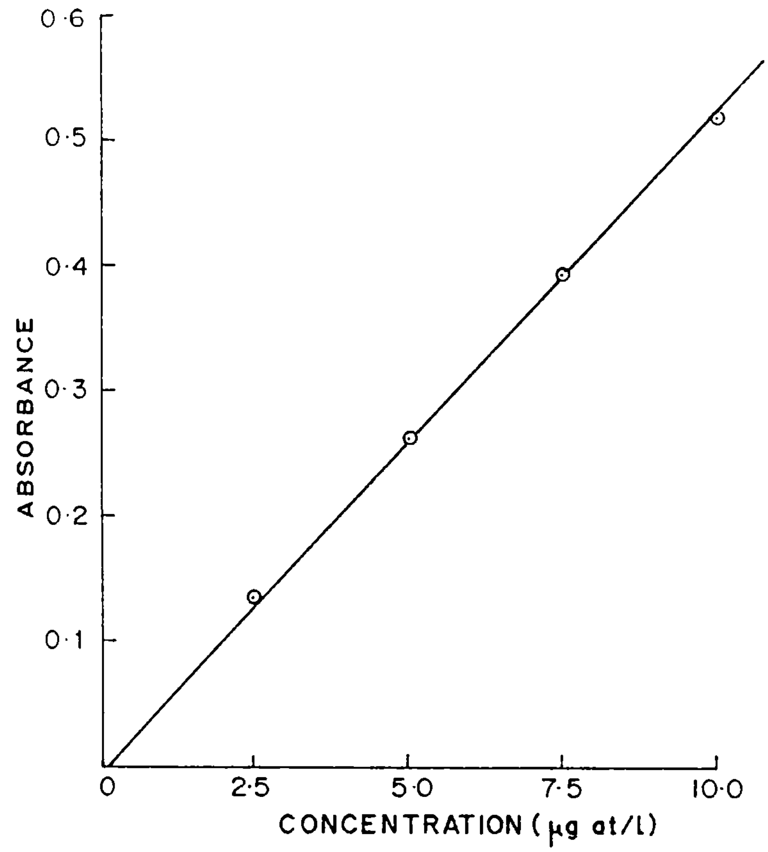


Fig. 2.4. Calibration curve for total N

Table 2.4.1. Percentage recovery of total-N from glycine standards using the oxidation procedure.

Standards used (ugat/l N)	Absorbance	Concentration estimated (ugat/l)	% recovery of total-N
5.0	0.210	4.72	94.4
10.0	0.438	9.90	99.0
20.0	0.871	19.57	97.8
30.0	1.280	28.80	96.0
40.0	1.602	36.00	90.0
50.0	1.980	44.55	89.1

pore water was carefully collected in specimen tubes and were diluted with distilled water as the quantity obtained were insufficient for various analyses. Ammonia, nitrite, nitrate and inorganic phosphate were estimated for a selected set of samples using the standard procedures as discussed earlier.

2.4.4. Sediment samples

Eh of the sediment samples were determined using a platinum electrode attached to a portable pH meter (PHILIPS, Model pp 9046) after proper calibration.

The sediment samples were dried in a hot air oven around 70°C in glass petri dishes. The dried samples were homogenized and a portion of it was ground to a fine powder in a porcelain mortar. Another portion of the sample was used for grain size determination. Percentage of sand, silt and clay portions was determined by sieving through a net of 64 μ mesh size and pipette analysis as described by Krumbein and Pettijohn (1938).

The powdered samples were analysed for total nitrogen and phosphorus contents. Total nitrogen in the sediment samples were determined by the semi-micro Kjeldahl method (Bremner, 1965). For the determination of total phosphorus, the sediment samples were digested according to Rochford (1951) and the orthophosphate estimated as described earlier (Section 2.4.2.(f)).

2.5. Data Presentation

The data obtained from the field observations and laboratory studies were processed and presented in this thesis under various sections. The methods employed for the presentation of these results are summarised here.

2.5.1. General distribution

The spatial distribution of all the parameters studied are represented by contour lines (vertical profiles) for each month of observation. The contour lines are based on the tidally averaged surface, mid-depth and bottom values of the respective parameter in the water column. Average values of two stations were taken to represent a particular cross-section.

Seasonl changes of salinity and nutrients are represented by integrated mean values in which each value represent 42 data points. ie., 7 observations at 3 depths in each of the two stations in a cross-section.

The period of study is divided into three seasons: postmonsoon (October to January), premonsoon (February to May) and monsoon (June to September). Tidal variations and inter-relationships of various parameters were analysed, taking a representative month for each season, viz., December for postmonsoon, March for premonsoon and July for monsoon. The same method was followed for describing the distribution of urea-N and, nitrogen and phosphorus distribution in sediments and interstitial waters of the estuary.

2.5.2. Inter-relationship between various parameters

Inter-relationship between various parameters at all depths, stations and seasons during a tidal cycle were studied using statistical methods. Following analyses were carried out on non transformed data:

i) Karl Pearson's coefficient of correlation between the parameters Ammonia-N, Nitrate-N, Organic-N, Inorganic phosphate, Organic-P and Salinity, and tested using 't' statistics,

$$t = \frac{|r|\sqrt{n-2}}{\sqrt{1-r^2}}$$

where, r = correlation coefficient and

n = number of observations.

ii) Three way analysis of variance to test the significance of difference between stations, seasons and depths and their interaction effects .

(Sokal and Rohlf, 1981).

2.5.3. Estimation of nutrient fluxes

Nutrient fluxes were calculated from velocity and nutrient concentration as given in Stern et al.(1986), with some modifications. Instead of the centre point observation in Stern et al.(1986; 1991), sampling was done at two stations in a cross-section and at three depths (surface, mid-depth and bottom) at each station in the present study.

The seaward and landward vectors of riverflow at each sampling depth was multiplied by the respective nutrient concentration and averaged for the water column to get the instantaneous flux. The net fluxes are the algebraic sums of the instantaneous fluxes over the tidal cycle sampled divided by the number of observations in the tidal cycle. Net fluxes for all the stations and their cross-sectional averages for each of the four sections were calculated (using a FORTRAN computer program) and presented as flux per m^2 of cross-sectional area per second.

Material transport through a particular cross-section was obtained by multiplying the average of the net fluxes by the mean cross-sectional area. Changing cross-sectional area due to changing water level was also taken into account in the calculations. Fluxes of particulate and dissolved nutrients were not measured separately, so the fluxes discussed here will represent the sums of particulate and dissolved fractions. The positive sign indicates transport towards the sea and the negative sign transport towards the river.

CHAPTER 3

GENERAL HYDROGRAPHY

3. GENERAL HYDROGRAPHY

The environmental conditions of the estuaries of South-West and South-East coasts of India are largely governed by two dominant factors, namely tides and seasonal changes induced by the monsoonal cycle. These coupled with various physico-chemical and biological factors contribute largely to the variability of the estuarine environment.

Chaliyar river estuary of Malabar Coast is well known for its aquatic resources and is an important estuarine system. Studies on the hydrography of this estuary are limited to the works of James and Sreedharan (1983), Premchand et al.(1987), Giridhar Hadnooker et al.(1987), and Nirmala et al.(1990). But in none of the above studies there is systematic monthly data collection with tidal changes.

In this chapter, the temporal and spatial variations of different hydrographic parameters like temperature, salinity, pH and dissolved oxygen of the system during the period of study are discussed. Tidal variations are analysed to investigate the extent to which the tides affect these parameters. Details regarding the sampling procedure and the methods employed are discussed in Chapter 2.

3.1. Temperature

Temperature is subjected to change in estuarine waters, where it is influenced by seasonal as well as diurnal changes in air temperature and the temperature of adjacent sea water and river water. Temperature in shallow estuaries change relatively fast compared to the open sea and the extremes are separated by a larger amplitude than in the sea. According to Klein (1962) the direct effect of temperature as an environmental factor is difficult to assess because in stream's environment it is often linked with the speed of the current and type of bedcooler waters usually being associated with the shallow depths more common in the upper reaches of rivers.

Temperature effects on water quality can be of three types; physical, chemical and biological. Temperature affects the physical properties of water such as density, viscosity, vapour pressure, surface tension, gas solubility and gas diffusion. Temperature rise can cause stratification in ambient water; causing the overflow or underflow of the incoming water of different density. Chemically temperature affects not only the rate of reaction but also the extent to which the reactions takes place. Further, water temperature - the easiest physical measurement - shows more significant variations seasonally than spatially and it is correlated with salinity and density.

Fig 3.1 depicts the monthly spatial distribution of temperature in the estuary during the period of study. The results showed an increasing trend from the mouth towards upstream during postmonsoon months (Oct-Jan). The values ranged from 29.0 to 31.5°C at the surface and 28.5 to 31.3°C

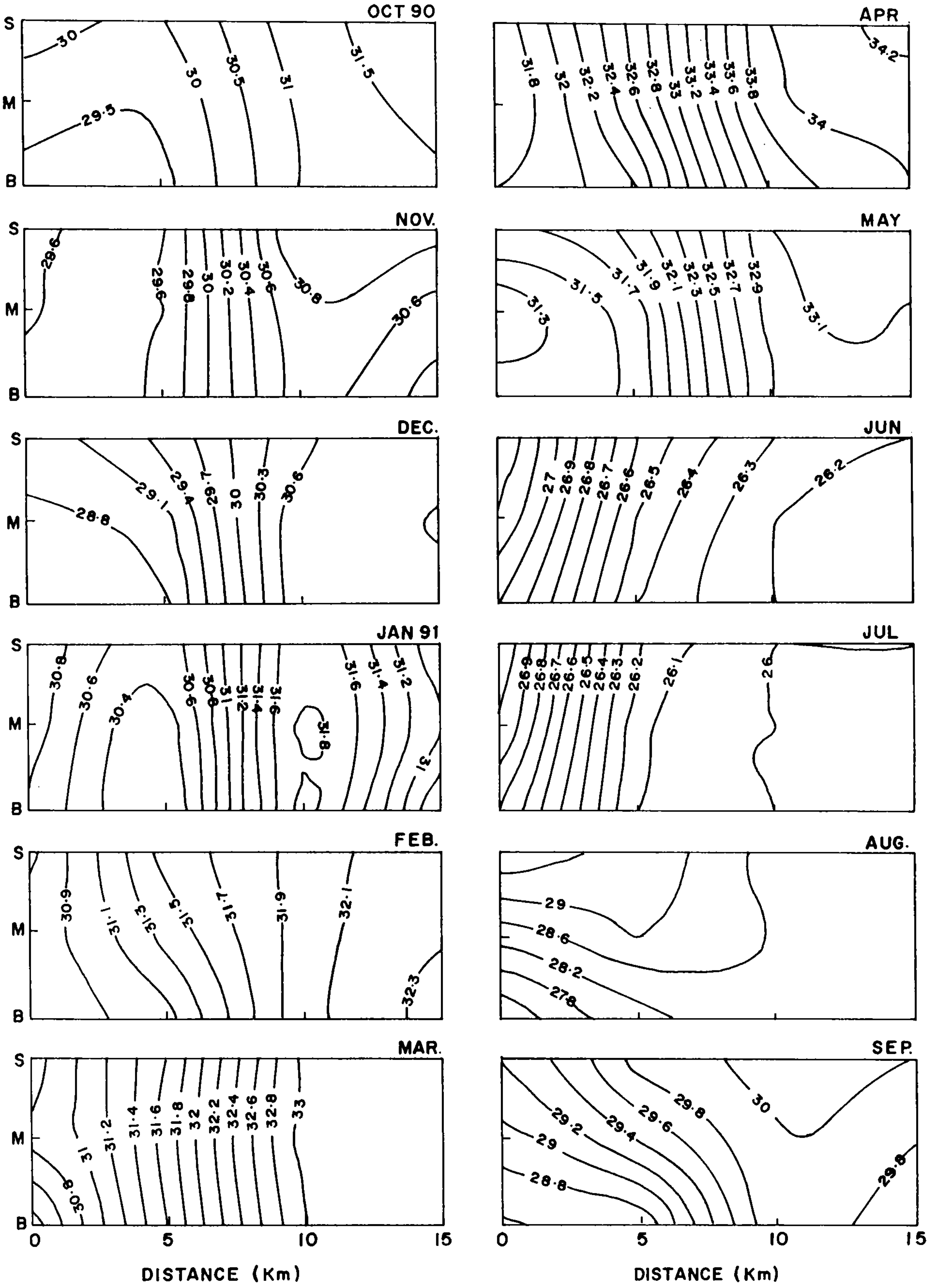


Fig. 3·1· SPATIAL VARIATIONS IN TEMPERATURE DURING EACH MONTH OF OBSERVATIONS in the bottom. November and December showed comparatively cooler waters upto 5 km and uniformly higher temperature maintained thereafter. But in January uniform high values were noticed. The difference between surface and bottom temperature was less than 1°C during this period. The horizontal distribution of temperature during pre-monsoon period (Feb-May) exhibited a temperature variation from 30.7 to 34.2°C at the surface and 30.4 to 33.9°C at the bottom. The vertical gradient was less than 1°C. The distribution showed a uniform pattern of increase from the barmouth towards upstream during this season.

A decrease in temperature was observed during monsoon and the lowest values (<27°C) were in the months of June and July. The distribution was almost uniform throughout the estuary. During August and September low water temperature was noticed at section 1, and relatively high and more or less uniform distribution at the upstream sections. During August, the surface temperature at section 1 was 29.8°C whereas at the bottom it was only 27°C, showing a vertical gradient of 2.8°C.

Temperature of the estuarine waters showed very little variation with tide except during monsoon. During monsoon, tidal influence was marked only at section 1 and the variations followed the tidal rythm. Tidal variation of temperature at section 1 during July is shown in Fig.3.2.6. The mean temperature during the tidal cycle showed a difference of 2°C at the surface and 3°C at the bottom near the river mouth and the corresponding temperature difference for upstream sections were found to be less than 1°C. The average value of 7 observations in the water column during the tidal cycle showed high values (>31°C) during April-May and lower values (<27°C) during June-July. The upper zone recorded peak value of >34°C and lowest value of <27°C in the corresponding months. The annual variation in temperature was 8.2°C and the maximum vertical gradient observed was 2.8°C during August.

Compared to temperate estuaries, the annual variation in temperature was found to be less in tropical estuaries. Lack of vertical stratification in temperature was reported by Qasim and Gopinathan (1969) for Cochin backwaters due to shallow nature. However Shynamma and Balakrishnan (1973) noted prominant vertical stratification in temperature in Cochin estuary at 8m depth. Chandran and Ramamurthy (1984) observed maximum fluctuation of 3.5°C at the surface and 4°C at the bottom in Vellar estuary.

Premchand et al. (1987) noticed a vertical gradient of >6°C at Beypore barmouth during monsoon. But during pre and post monsoon seasons they noticed negligible difference between surface and bottom temperatures. Nirmala et al.(1990) noticed a decrease in temperature from the salinity zone towards upstream in the Chaliyar river estuary.

Low water temperature observed in rivermouth during August is due to the cloudy nature of the sky and the intrusion of dense and comparatively cooler water from the sea. Dense, low oxygenated cold water is present on the shelf during this season (Sharma, 1968). The freshwater inflow through the river and intrusion of seawater with tide have profound influence on the distribution of temperature in the estuary. Similar feature was observed by Sankaranarayanan and Qasim (1969) in the Cochin estuary and Ramamirtham and Rao (1973) along the west coast of India . Higher temperature and less vertical gradient observed in the upper reaches could be due to shallow nature of the estuary.

3.2. Salinity

Salinity has been recognised as an important parameter in studying the physico-chemical characteristics of estuaries. The salinity distribution in an estuary is mainly governed by factors such as seawater intrusion, river discharge, rainfall and evaporation. The mixing and diffusion phenomena occurring in estuaries are largely influenced by salinity distribution pattern. The relationship with salinity and other physico-chemical parameters such as temperature, pH and dissolved oxygen is important. Estuaries are often classified according to salinity distribution. The salinity characteristics of an estuary depend to a great extent on forces such as pressure gradient, field acceleration, coriolis force, interfacial friction etc. acting on it. Thus in understanding the different processes taking place in an estuary, a study of the salinity distribution during different seasons of the year is a pre requisite.

Fig 3.2.1. shows the seasonal variation in the integrated mean values of salinity at four sections in the Chaliyar river estuary during the period of observation. The vertical salinity profiles illustrating the spatio-temporal variations during different months of the year is shown in Fig 3.2.2. The salinity values plotted are the mean values of the hourly observations in a tidal cycle.

The vertical profiles of salinity for October and November showed a similar pattern of distribution when the estuary was freshwater dominated beyond 10 Km from the river mouth. The lower 8 Km of the estuary was highly stratified with a vertical salinity gradient of 15×10^{-3} at the river mouth and about 20×10^{-3} at Section 2 (5 Km down stream). Stratification increased during November and the gradients were 18×10^{-3} at the river mouth section and 22×10^{-3} at section 2. This being a period of moderate river discharge, salinity intrusion due to tidal forcing was noticed upto a distance of about 10 Km from the rivermouth. During December because of the decrease in river discharge and an increase in tidal forcing, salinity in the estuary increased with less stratification. Maximum stratification observed during this period was in the 5-10 Km region of the estuary with a vertical gradient of 8×10^{-3}.

A further increase in salinity with very less vertical variation ($<2 \times 10^{-3}$) was observed during January.

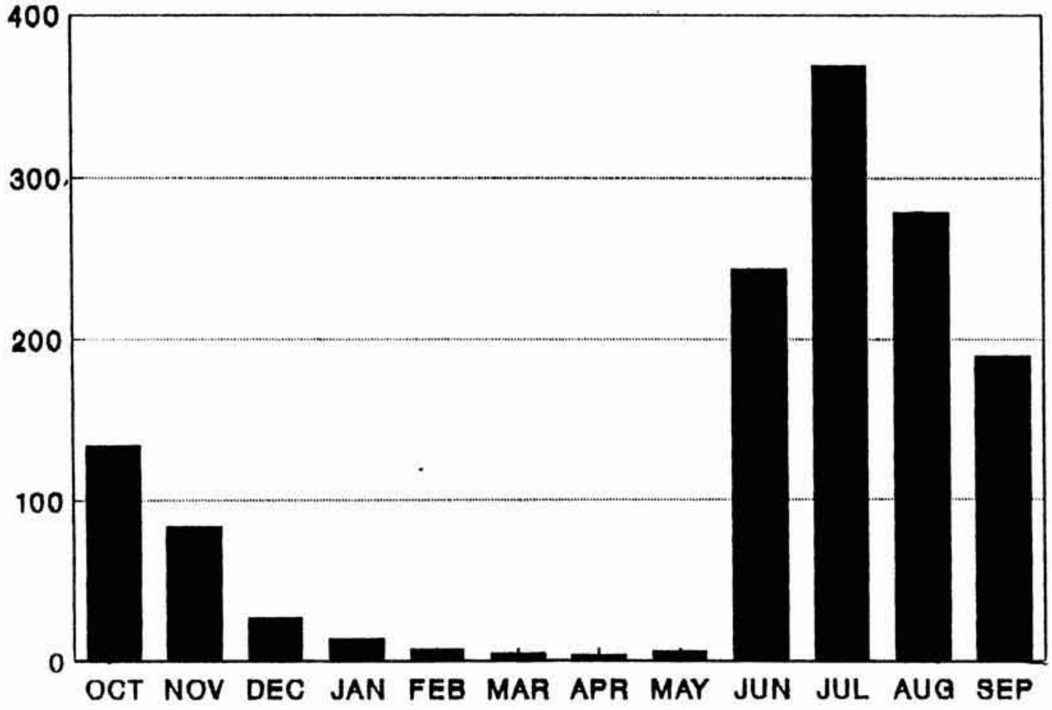


Fig.3.2. Monthly mean river discharge ($m^3 s^{-1}$) through Chaliyar. Decinial average for 1980 - 1990. (Data from Central Water Commission, Hyderabad.)

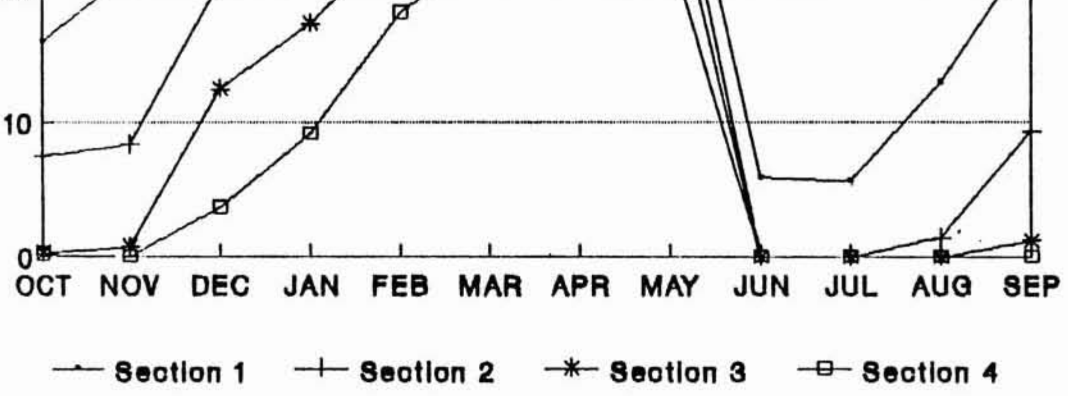


Fig.3.2.1. Seasonal changes of the integrated mean values of salinity (X 10^{-3}) at four sections in the estuary.

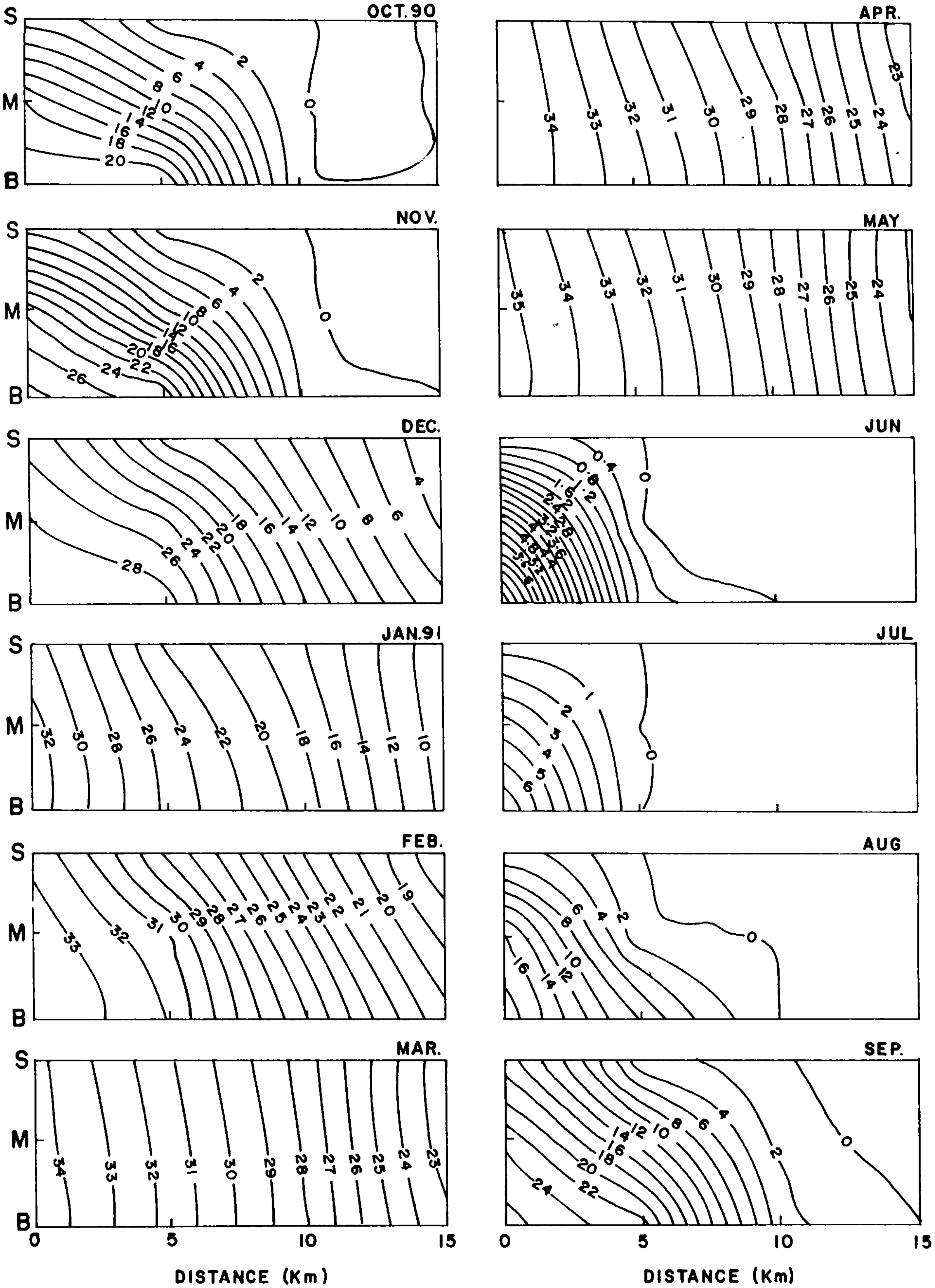


Fig. 3·2·2 SPATIAL DISTRIBUTION OF SALINITY DURING EACH MONTH OF OBSERVATION

Horizontally salinity decreased from a mean value of 32×10^{-3} at the river mouth to 10×10^{-3} at the upstream section. Intrusion of saline water increased to a greater extent during February with a vertical gradient of about 3×10^{-3} throughout the estuary. Salinity values ranged between a mean value of 33.5×10^{-3} at section 1 and 19×10^{-3} at section 4. The entire portion of the estuary was marine dominated during the pre monsoon months, March to May. High salinity values with very little fluctuations with tidal changes and a vertically homogenous water column suggests a well mixed condition during this period. Salinity values varied between 34×10^{-3} and 35×10^{-3} at the river mouth section and it gradually decreased to 23-24 $\times 10^{-3}$ at the upstream section.

During June-July, salinity values suddenly dropped to zero except at the river mouth where saline water intrusion was observed at the time of high tide. Mean salinity values at the river mouth section varied between 0.5 and 8×10^{-3} in the water column and the tidal limit during this period was observed to be 5km from the mouth. Heavy rainfall and consequent fresh water runoff caused the entire estuary to be freshwater dominated during this period. After the heavy runoff period, salinity gradually increased in the estuary during August. The vertical profiles (Fig.3.2.2) for August showed a highly stratified condition in the lower 5 Km of the estuary with a vertical gradient of 15×10^{-3} at section 1 and 7×10^{-3} at section 2. The increase in salinity observed at the lower sections especially at the bottom during this period of high river discharge could be due to the intrusion of upwelled water (see Section 3.1.). During September, a further increase in salinity values and stratification was observed upto a distance of 10Km from the rivermouth. Maximum stratification with a vertical gradient of 18 X 10^{-3} was observed at section 2. Stratification was less at the river mouth because of the increased tidal mixing there and the vertical salinity gradient was less than 10 X 10^{-3} during this period.

The variations in salinity during a tidal cycle was found to follow the tidal rythm. During the flood tide, salinity increased and during the ebb tide it decreased. During the monsoon months of June and July, tidal influence was noticed at section 1 only where high saline water was found at the bottom (26-28 X 10^{-3}) and mid-depth (12-17 X 10^{-3}). Due to the high fresh water run off, salinity was nearly zero at the surface throughout the tidal cycle. In the post monsoon season (Fig 3.2.4) significant variations in salinity from surface to bottom during a tidal cycle was observed throughout the estuary. Section 1 showed comparatively smaller vertical gradients (2 - 6 X 10^{-3}) and the upstream sections were highly stratified with a maximum vertical gradient of 15 X 10^{-3}, especially during the high water regime. A gradual fall of salinity was observed during ebb period and there was a gradual increase during flood period. During pre monsoon, a nearly marine condition with high and uniform salinity was observed at section 1 and

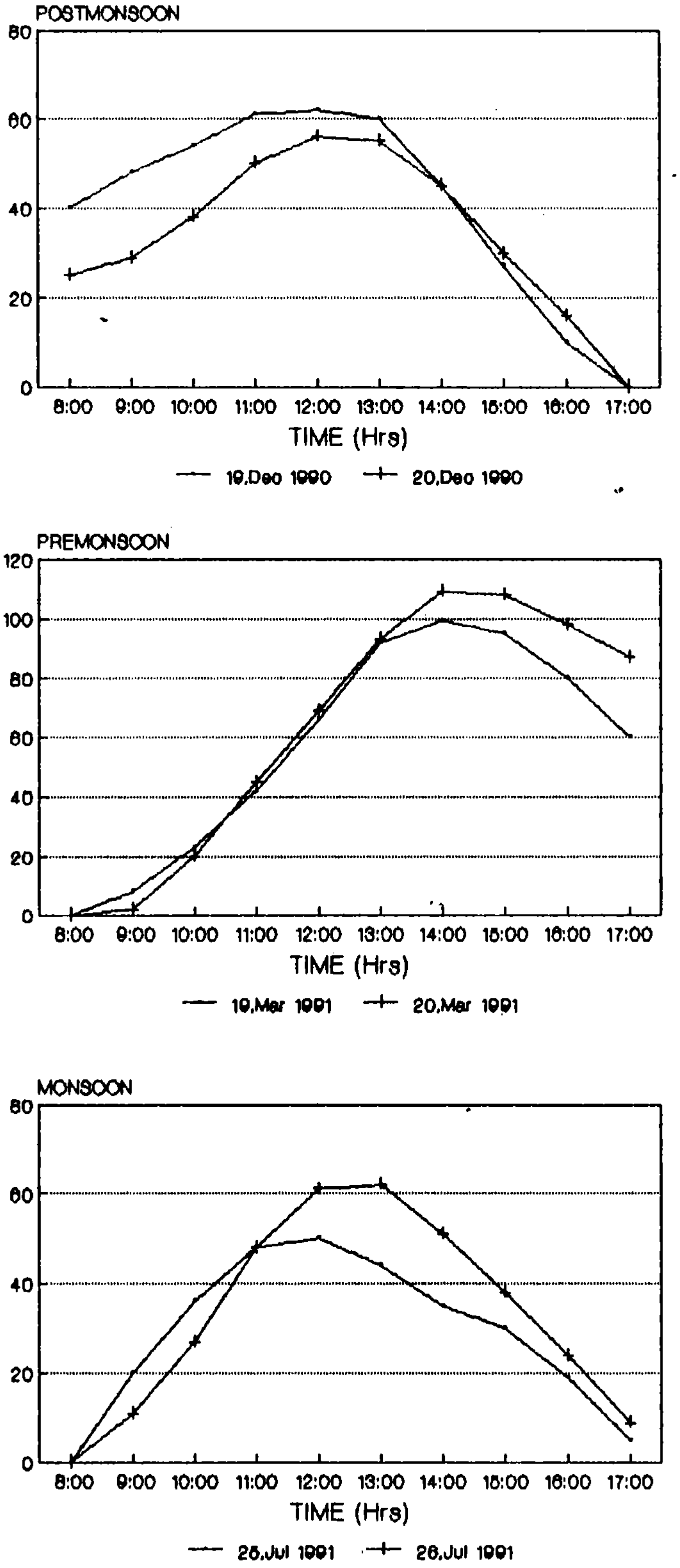


Fig.3.2.3. Water level variation (cm) with tide at section 1 in the representative days of observation during postmonsoon, premonsoon and monsoon. (Data from Port Authorities, Beypore.)

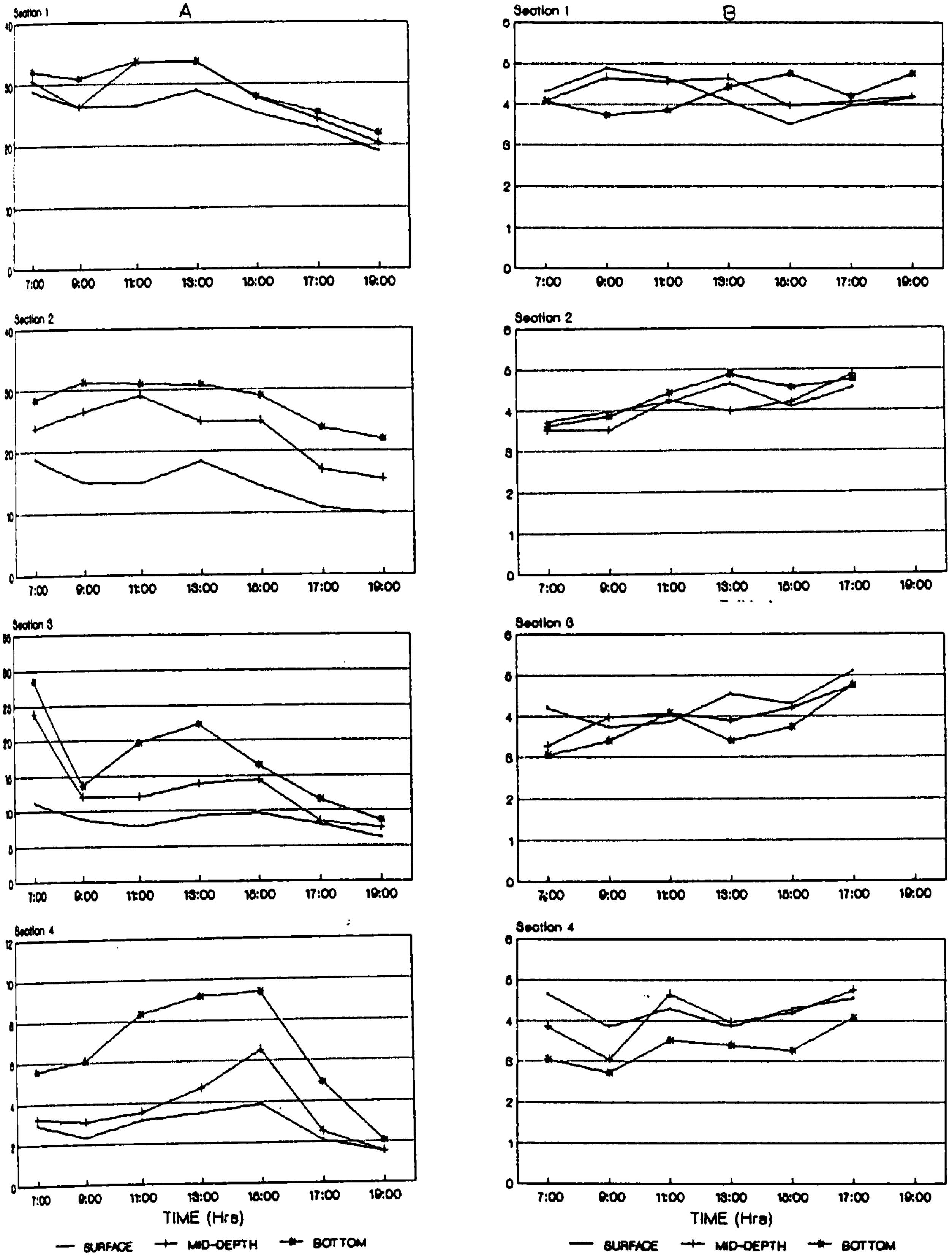


Fig.3.2.4. Tidal variations in salinity (A) and dissolved oxygen (B) during post monsoon.

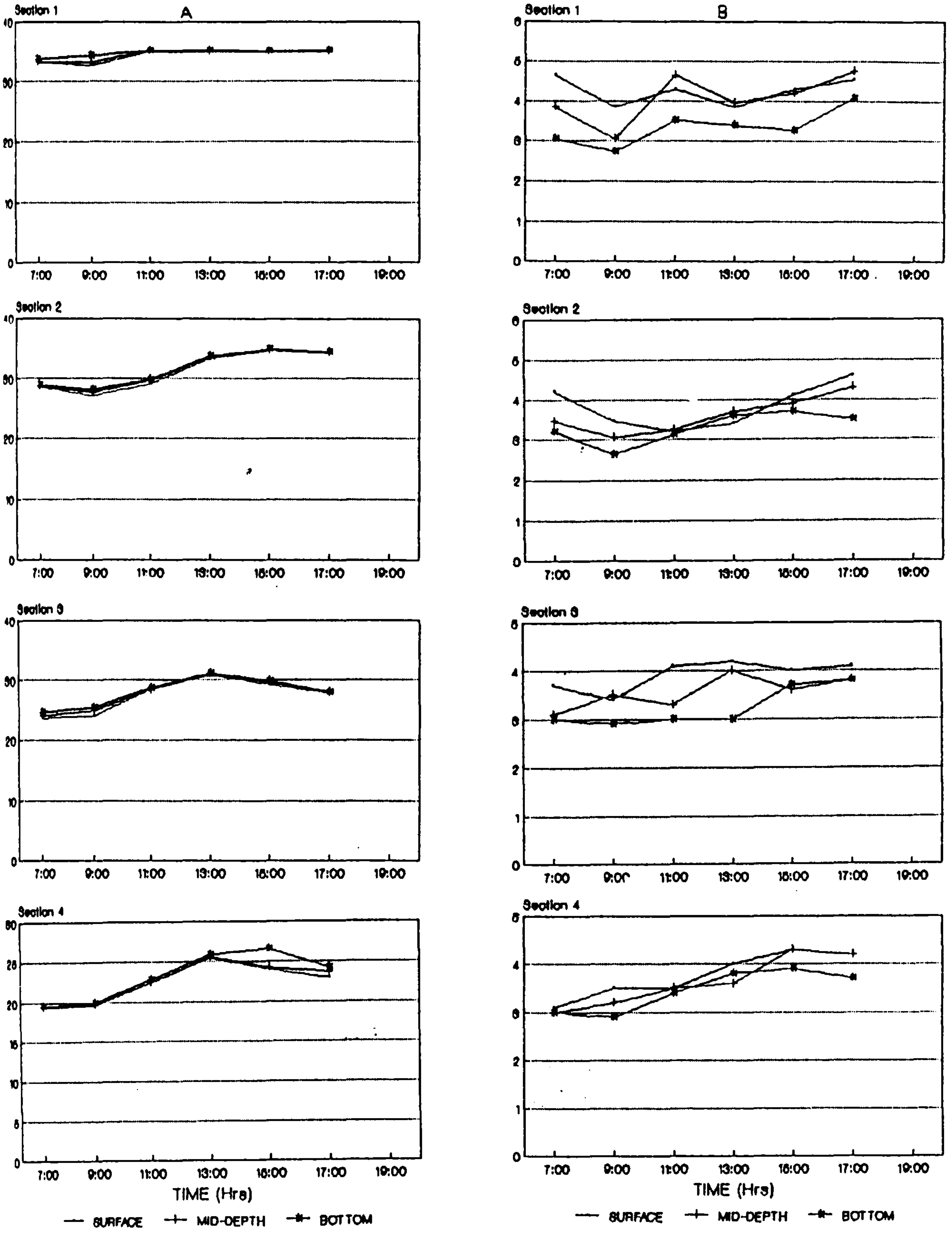


Fig.3.2.5. Tidal variations in salinity (A) and dissolved oxygen (B) during pre monsoon.

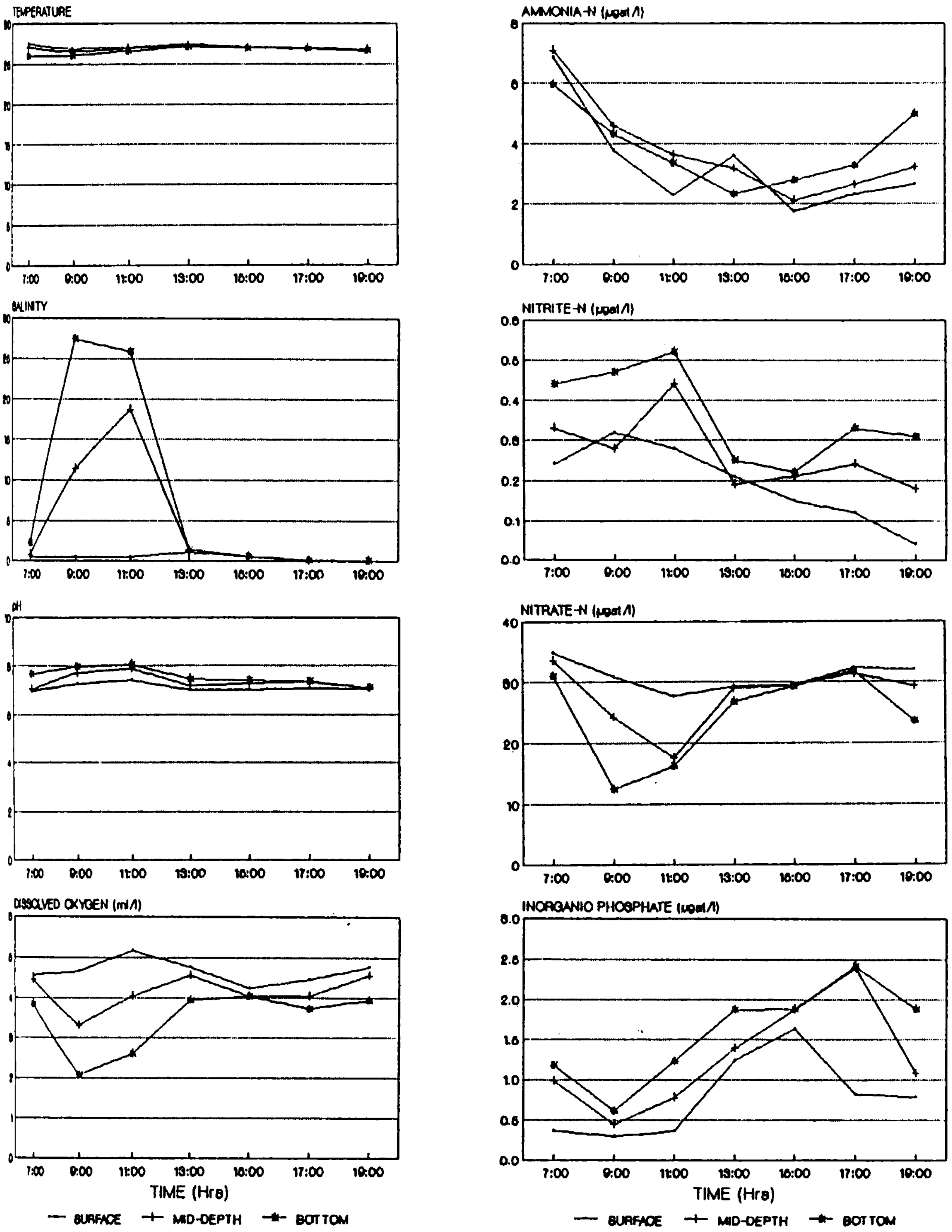


Fig.3.2.6. Tidal variations of various physico chemical parameters at section 1 during monsoon.

variations in the upstream sections exactly followed the tidal rythm. Almost well-mixed condition throughout the estuary and salinity value as high as 26.5 X 10^{-3} at section 4 during the flood period were indicative of strong tidal currents during this period.

The results of the present study are comparable with the observations of several workers in the same estuary and other estuaries along the south-west coast of India. During heavy monsoon months salinity was limited to 5Km from the rivermouth as noticed by Nambudirippad and James (1987) and Nataraj et al. (1987). Intrusion of sea water was found even upto 28Km from the river mouth during the premonsoon period (James and Sreedharan, 1983). Premchand et al. (1987) reported the absence of saline water in this estuary during June-July and observed high salinity during August which they attributed to the intrusion of upwelled water. But the present observations indicate the presence of saline water at the bottom (Fig.3.2.2) even up to 5Km from the river mouth during June-July at the time of flood tide.

Several workers (Haridas et al., 1973; Cherian et al., 1975; Balakrishnan and Shynamma, 1976) have reported wide fluctuations in salinity of tropical estuaries due to extreme conditions of drought and monsoon affecting the estuarine environment. Saraladevi (1986) and Nair et al. (1988) observed wide range of variarion (0.24 to 31 X 10^{-3}) in salinities, which was found to be controlled by tidal and monsoonal flow and by shallowness of the area.

The extent of salinity intrusion during different seasons have also been reported from many estuaries. A salinity wedge extending upto a distance of 10 km was observed in the Mandovi and Zuari estuaries during monsoon (Qasim and Sen Gupta, 1981). A distinct seasonal pattern of salinity in the Ashtamudi estuary with highest values during premonsoon and declining values from estuarine mouth to the riverine zone was reported by Nair et al. (1983). Sankaranarayanan et al. (1986) observed salinity intrusion upto 25 Km in the Periyar river estuary during premonsoon and upto 5 Km during monsoon. They noticed a vertical gradient of less than 3×10^{-3} during the pre and post monsoon periods and greater than 10×10^{-3} during monsoon.

In general, the pattern of distribution observed during the present study in the Chaliyar river estuary showed a similar trend as in other estuaries. The important factors affecting the salinity distribution in the estuary are tidal incursion through the barmouth and rain fall and consequent river discharge. During the monsoon months when the fresh water discharge was maximum, sea water influence was felt upto 5 Km from the river mouth at the bottom with salinity as high as 32×10^{-3} at river mouth during high tide. During the post monsoon months the high saline water extends upto 10 Km upstream. The absence of vertical salinity gradient during summer with minimum river discharge showed the prevalence of well mixed condition probably enhanced by strong tidal currents as stated by Bowden (1967). Thus, the estuary varies from a salt wedge type during monsoon to an intermediate partially mixed type during postmonsoon to a well mixed type during pre monsoon season.

3.3. pH

The hydrogen ion concentration (pH) of water is an important indicator of the chemical conditions of the depositing environment. It shows whether the water is acidic or alkaline in nature. The ranges of pH expected for normal sea water is 8.0 to 8.3, for coastal waters it is 7.9 to 8.2, and it varies widely in esturies. In the estuarine waters, pH values are mainly affected by river discharge, sea water intrusion and anthropogenic influences. The processes of primary production, respiration and mineralization of organic matter are also able to alter the pH of the system because they can cause significant changes to the oxygen and carbondioxide concentrations of aquatic environments. Gnaiger et al. (1978) suggested the involvement of photosynthesis in determining pH. Toxicity of ammonia as well as its oxidation to harmless compounds by bacteria is pH dependent.

Fig.3.3. illustrates monthly spatial distribution of pH in the estuary during the period of investigation. The values ranged between 6.0 and 7.9 during October, the values being high in the lower reaches of estuary. In November the estuarine mouth showed a high value of 8.1 and reduced to 7.5 upto 10km from the mouth and decreased to 7.1 in the upper region. During December high pH (8.0 to 8.2) was observed

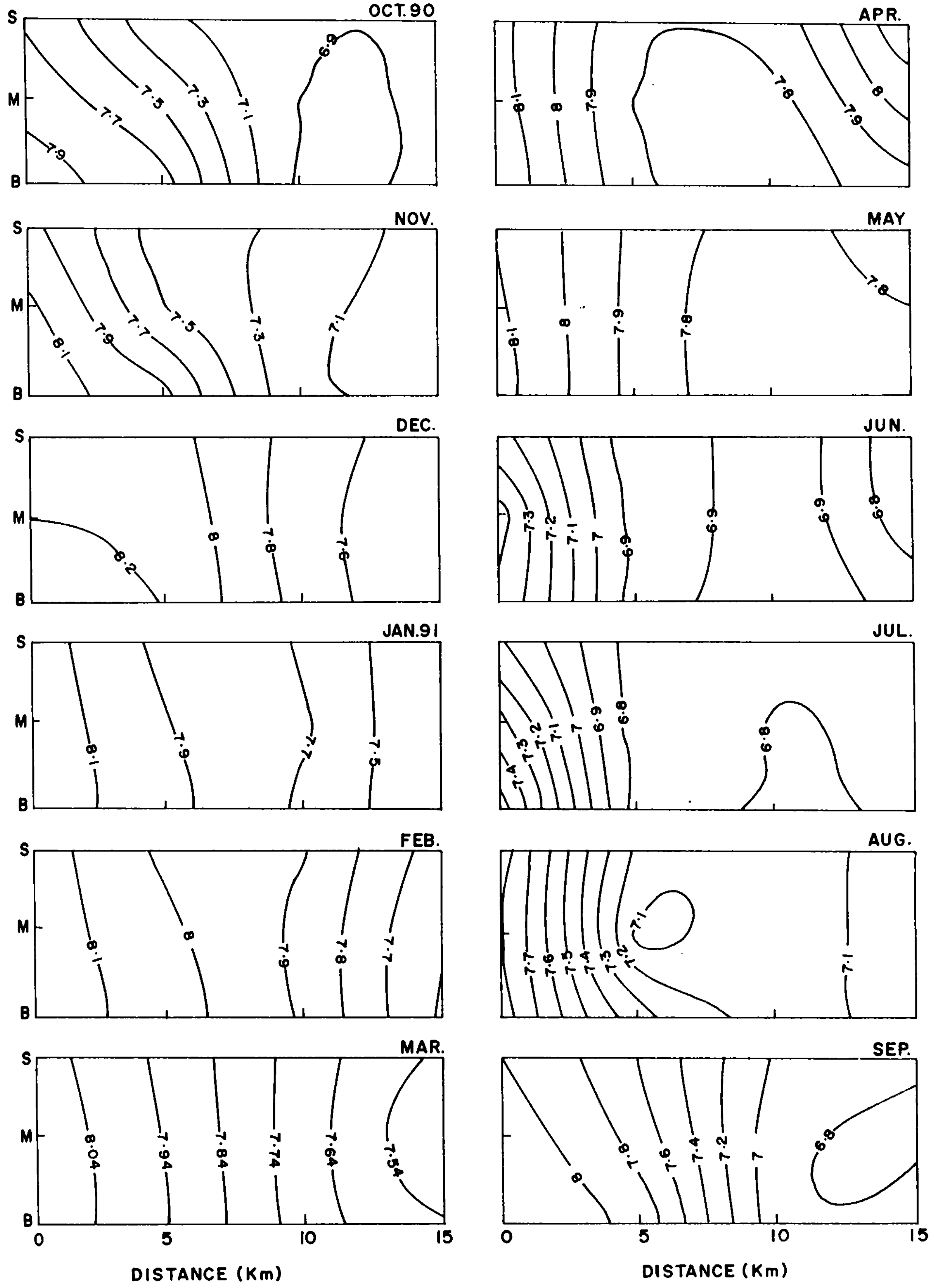


Fig.3.3. SPATIAL VARIATIONS IN pH DURING EACH MONTH OF OBSERVATION

upto about 7km and it ranged between 7.6 and 7.8 in the upstream. Thus pre monsoon months showed higher pH in the estuarine waters and declined thereafter. The horizontal distribution of pH value was between 6.9 and 8.2 during this season. The high values observed were in the lower reaches and it decreased towards upstream of the estuary. The values varied between 7.5 to 8.4 throughout the observation period. Monsoonal values were lower compared to other seasons and also showed the same trend with high pH in the estuarine region and low in the upper freshwater zone. The values were within the range of 6.7 to 7.8 except during September when the pH increased to 8.

In general, monsoon months recorded low pH values and pre monsoon high values especially in the lower reaches of the river. Not much variation was noticed between surface and bottom values. The tidal average for the water column ranged between 6.9 and 8.25, 7.3 and 8.4, and 6.7 and 7.85 during the post monsoon, premonsoon and monsoon respectively. Nair et al. (1983) observed a clear decrease in pH from the marine to freshwater zone in the Ashtamudi estuary. The tidal and diurnal variations in pH fluctuated from 7.75 to 8.25 and 7.72 to 8.35 in Vellar estuary (Chandran and Ramamoorthy, 1984). A pH range of 6.9 - 8.23 in Kayamkulam estuary was reported by Ananthakrishnan et al. (1990). Nair et al (1988) recorded a low pH value during monsoon months in Cochin backwaters. Saraladevi et al.(1983) have reported for Beypore estuary an average pH value of 7.66 and 7.75 during pre monsoon, 6.35 and 6.53 during monsoon and 6.68 and 7.63 during post monsoon for the surface and bottom waters respectively.

The distribution of pH clearly indicated that the low pH values especially at the surface during the monsoon months are due to heavy fresh water discharge and the increased pH values observed as the season progressed are due to higher sea water incursion. Similarly there was a gradual decrease in pH values towards upstream which showed the influence of the sea water on pH. The relatively higher pH values recorded during the pre and post monsoon months may be due to the removal of carbon dioxide by photosynthetic activity which is higher during these periods.

3.4. Dissolved Oxygen

Studies on dissolved gases help in understanding physical, chemical and biological processes taking place in natural waters. Dissolved oxygen in the estuarine environment is chiefly controlled by tidal ingress, freshwater runoff and water temperature.

The vertical profiles (Fig.3.4) shows the temporal and spatial distribution of dissolved oxygen in the estuary. Except for October which recorded lower values (3.0 - 3.5 ml/l) upto 7km from the river mouth, the dissolved oxygen concentrations were higher during other months of post monsoon season. The tidal variations during the post monsoon

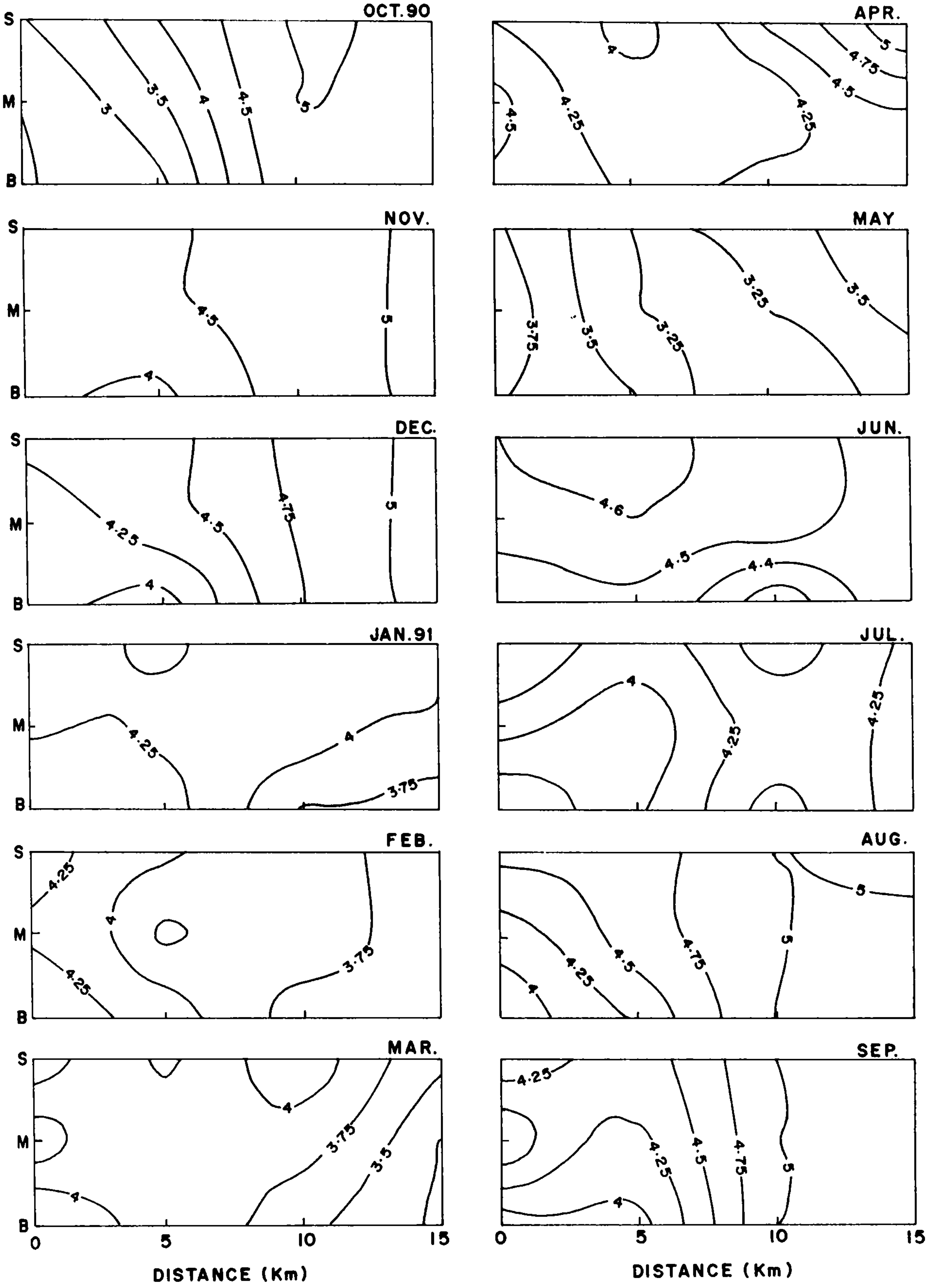


Fig. 3·4· SPATIAL VARIATIONS IN DISSOLVED OXYGEN DURING EACH MONTH OF OBSERVATION season (Fig.3.2.4) showed no definite pattern.

In the pre monsoon months of January to March, oxygen values were higher at the barmouth (4.0 - 5.0 ml/l) and lower (<4.0 ml/l) towards upstream. But in April values again increased throughout the study area. Contrary to this, in the month of May lower values ranging between 3.25 and 3.75 ml/l were observed. In general oxyty values were lower in premonsoon compared to postmonsoon and monsoon months. Tidal variations (Fig.3.2.5) showed an increase in dissolved oxygen values during the flood period and lower values during the ebb period.

June to September exhibited more or less uniform horizontal distribution having a range of 4.25 to 5.0 ml/l. Tidal variations during July (Fig.3.2.6) showed very low oxygen values at the bottom during flood tide. Tidal mean fell within the range of 2.98 - 5.35 ml/l at the surface and 2.47 - 5.24 ml/l at the bottom in the study area. Lower oxygen values (< 3.0 ml/l) observed at the bottom during the months of July and August are due to the incursion of high density low oxygenated upwelled water present in the coastal region during these months. Upwelling during the south-west monsoon has been reported by several workers (Banse, 1959; Ramamirtham and Rao, 1973; Sharma, 1978) along this coast. Premchand et al.(1987) observed oxygen values of 2.52 to 6.0 ml/l during August in Beypore barmouth. Similar feature has been reported earlier from other estuaries also (Ramamirtham and Jayaraman, 1963; Sankaranarayanan and Qasim, 1969;

Sankaranarayanan and Jayaraman, 1972).

Although vertical differences in oxygen values were not conspicuous due to the shallow nature of the estuary, the surface values showed slight increase than the bottom values. In general, dissolved oxygen was higher during monsoon and comparatively lower during certain months of pre and post monsoon seasons. This may be due to the oxidation of organic matter at intermediate levels. Low oxygen values during March and May in the present study could be attributed to the low fresh water flow during the pre monsoon and also to higher utilisation by organic matter.

It was reported earlier that dissolved oxygen shows inverse relationship with salinity, with high values during flood tide and low values during ebb tide (Qazim and Gopinathan, 1969; Dehadri, 1970; Vijayalakshmi and Venugopalan, 1973). In the present study, tidal variations indicate that the inverse relationship is true during monsoon and post monsoon seasons while a direct relationship exist during the premonsoon.

Nair et al. (1984) noticed oxygen values ranging between 3.68 -7.29 ml/l at Neendakara, 3.05 -6.04 ml/l at Kayamkulam and 2.88 - 6.50 ml/l at Kadapuzha estuaries in the South Kerala coast. This high concentration of dissolved oxygen was attributed to the high rate of primary production by phytoplankton and benthic algae which could also be augmented by wave action enhancing the rate of solubilisation of atmospheric oxygen. According to Burton (1979), photosynthetic production of oxygen in estuarine waters alone averages at a rate of 1000g $m^{-2}year^{-1}$, a value about 4 times its globally averaged river input of oxygen in estuaries.

De Souza and Sen Gupta (1986) noticed a super saturation with respect to oxygen in the upper reaches of Mandovi estuary due to high photosynthetic activity in addition to the supply of oxygen by freshwater from numerous streams discharging into the estuary. Undersaturation in the lower reaches was explained by the reduced photosynthetic activity because of the high turbidity in the estuarine mouth. Chaliyar river mouth is subjected to intense fishing and other human activities which will increase the turbidity thereby reducing photosynthetic activity. The pattern of distribution of dissolved oxygen was similar to the pattern observed in other backwaters along south-west coast (Abdul Aziz and Nair, 1978; NIO,1982; Nair etal., 1983).

CHAPTER 4

NUTRIENT CYCLES

4. NUTRIENT CYCLES

4.1. THE NITROGEN CYCLE

Nitrogen occurs in the biosphere in a variety of forms ranging in oxidation states from +5 to -3. Inorganic forms include nitrate, nitrite, ammonia, molecular nitrogen and some intermediate gaseous oxides of nitrogen. Naturally occurring organic nitrogen consists primarily of amino and amide nitrogen along with some heterocyclic compounds such as purines and pyrimidines (Brezonik, 1972). Nitrogen compounds are present as cellular constituents, as non-living particulate matter, as soluble organic compounds and as inorganic ions in solution. All these forms of nitrogen are interrelated by a series of biogeochemical processes involving nitrogen fixation, ammonification, nitrification and denitrification collectively known as the nitrogen cycle. The nitrogen cycle is dominated by reactions involving biological material. All the reactions in the series

N_2 ----> NH_3 ----> NO_2^- ----> NO_3^- ----> amino acids
----> proteins

and reverse reactions back to nitrogen can be carried out by micro-organisms. The various processes involved in the nitrogen cycle can be summarised as follows:

(i) Nitrogen Fixation:-

Nitrogen fixation is the conversion of atmospheric elemental nitrogen to combined forms of nitrogen which can be assimilated by plants for their growth. The natural fixation of nitrogen is carried out by micro-organisms, which may be free-living or symbiotic, all of which contain the enzyme nitrogenase (O'Neill, 1985). The free-living nitrogen fixers may be either bacteria or blue-green algae.

(ii) Ammonification:-

Ammonia is generated by heterotrophic bacteria as the primary end product of decomposition of organic matter, either directly from proteins or from other nitrogenous organic compounds. Although intermediate nitrogen compounds are formed in the progressive degradation of organic materials, these rarely accumulate and are deaminated rapidly by bacterial action.

(iii) Nitrification:-

Nitrification may be broadly defined as the biological conversion of organic and inorganic nitrogenous compounds from a reduced state to a more oxidised state. Of the numerous oxidation and reduction stages in the nitrogen cycle, initial nitrification by bacteria, fungi, and autotrophic organisms involves;

$$NH_4^+ + 1.5\ O_2 ===== 2H^+ + NO_2^- + H_2O$$

which proceeds as

$$NH_4^+ \text{ ----> } NH_2OH \text{ ----> } H_2N_2O_2 \text{ ----> } HNO_2$$

$$NH_4^+ \text{ --------------> } NO_2^-$$

$$NO_2^- \text{ --------------> } NO_3^-$$

Nitrification is inhibited by certain dissolved organic compounds, especially by tannins and tannin decompositional derivatives.Although this mechanism has been demonstrated only in soil systems, there is a strong possibility that an analogous situation exists in freshwater systems of high humic levels, where ammonia concentrations are higher (Wetzel, 1975).

(iv) Denitrification:-

Denitrification by bacterial metabolism is the biochemical reduction of oxidised nitrogen anions, nitrate-N and nitrite-N, in the oxidation of organic matter. The general sequence of events of this process is:

$$NO_3^- \text{---->} NO_2^- \text{---->} N_2O \text{---->} N_2$$

which results in a significant reduction of combined nitrogen that can, in part, be lost from the system if it is not refixed. The denitrification reactions are asssociated with the enzyme nitrogen reductase and cofactors of iron and molybdenum, and operate similarly under both aerobic and anaerobic conditions.

4.1.1. Nitrogen in the estuarine environment

Nitrogen is supplied in elemental and chemically combined forms to estuaries. The main form of combined nitrogen is dissolved nitrate, which is derived from rock weathering and drainage from agricultural lands where nitrogenous fertilizers are added to the soil to increase the crop production. Nitrate is also considered to be the most stable oxidation level of nitrogen in seawater (Grasshoff, 1983). It is an essential nutrient for the growth of many photosynthetic autotrophs and has been identified as the growth limiting nutrient. Natural level of nitrate reported in most estuarine waters range from 10 to 40 μgat/l and decreases to very low values in the marine end (De Souza et al., 1981; Sharp, 1983). Other important forms of nitrogen for biogeo-chemical processes in estuaries are nitrite, ammonia and dissolved and particulate organic nitrogen compounds. Nitrite is present in estuarine waters in generally low concentrations as an intermediate product of microbial reduction of nitrate or oxidation of ammonia and as an excretory product of plankton. In most estuaries except which are subject to large discharges of treated or untreated sewage, nitrite concentrations seldom account for more than 10% of total oxidised nitrogen (Head, 1985).

Nitrogen in living material is incorporated into a vast range of compounds ranging from simple amino acids containing a single nitrogen atom to complex proteins containing many thousands. On death or decay, these compounds are released to the surrounding water and become part of the organically bound nitrogen fraction of natural waters. Significant quantities of urea-N was also found to contribute to the dissolved organic fraction in estuaries. Urea in combination with ammonia and nitrate could be considered as rapidly recycled nitrogen potential for phytoplankton production (Verlencar, 1985).

Nitrogen supply to estuaries is important for primary production. The supply of total organic nitrogen is found to be as great as the inorganic nitrogen, but the organic nitrogen appear to be biologically active to some extent only. So the productivity of a given estuary may depend on very effective regeneration on a rapid time scale or the marine or riverine supply of new nitrogen (Aston, 1980). The role of nitrogen in estuarine water quality and in maintaining and enhancing estuarine productivity have stimulated the study of the various forms of this element in estuarine ecology. Several investigators have reported that nitrogen is the limiting nutrient to primary productivity in marine and estuarine systems (Ryther and Dunstan,1971; Keeney, 1973; Nixon, 1981; Fisher et al., 1982; Kemp et al., 1982; Nixon and Pilson, 1983; D'Elia et al., 1986).

The important processes involved in the biogeochemical cycling of nitrogen species include the processes of rapid turnover in the water column, such as uptake, remineralization and oxidation. In the sediments, the processes include burial, remineralization, biological uptake, oxidation, reduction and denitrification (Nixon and Pilson, 1983). The biological removal of nitrogen from estuarine waters may be achieved by sedimentation and burial. This process provides a nutrient rich detrital resource for benthic productivity, and stimulates bacterial growth at the water-sediment interface. The release of previously deposited nitrogen compounds from estuarine sediments is a possible source of nutrients for productivity in the overlying waters (Aston, 1980).

In most coastal environments, the vast majority of the recycled nitrogen released from sediments to water is in the form of ammonium (Kemp et al., 1990). A portion of this ammonium regenerated by the decomposition and deamination of organic matter is oxidised to nitrate before it can escape from the sediments. This nitrate may, in turn, be used as a terminal electron acceptor by denitrifying bacteria producing gaseous nitrogen and nitrous oxide essentially unavailable to most coastal phytoplankton (Howarth et al., 1988). Thus the coupled process of nitrification-denitrification represents a sink that shunts nitrogen away from recycling pathways (Jenkins and Kemp, 1984). These coupled processes are important in the nitrogen budget of estuaries where nitrogen losses via denitrification may account for half of the terrestrial inputs (Smith et al., 1985; Seitzinger, 1987).

Berounsky and Nixon (1985) calculated the net nitrification rates for an estuarine system. Their study illustrates the importance of nitrification in estuarine systems in influencing the concentrations of dissolved inorganic nitrogen species and in affecting the availability of oxygen and nitrous oxide associated with this transformation.

A study of the variations in concentration of different nitrogen species in time and space will provide an insight into some of the above processes controlling the distribution of nitrogen in the estuarine ecosystem. Such studies were

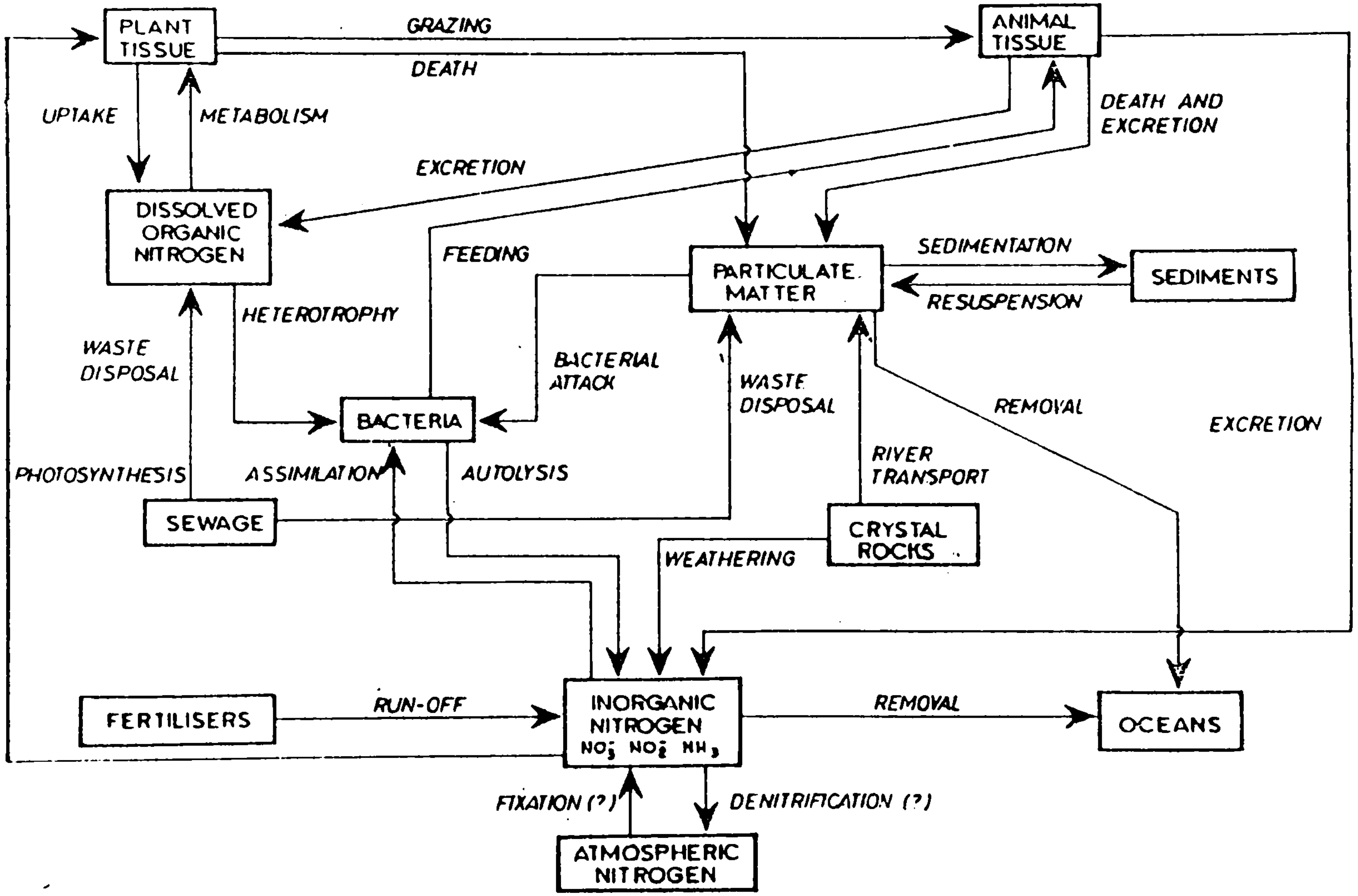


Fig.4.2.1. Nitrogen cycle in the estuarine environment.

carried out at Pamlico river estuary (Hobbie et al., 1975), Clyde estuary (Mackay and Leatherland, 1976), Mississippi river estuary (Ho and Barrett, 1977), Tamar estuary (Morris et al.,1981), Morlaix estuary (Wafar, 1981), Himmerfjard estuary (Wilmot et al., 1985) and Rhode river estuary (Jordan et al., 1991). Some of the Indian estuaries which have undergone such investigations are Cochin estuary (Sankaranarayanan and Qasim, 1969; Manikoth and Salih, 1974; Lakshmanan et al., 1987; Anirudhan, 1988), Mandovi-Zuari estuarine systems (De Sousa et al., 1981; De Sousa, 1983) and Mahanadi estuary (Sen Gupta and Upadhyay, 1987).

The general nitrogen cycle which describes the transformations of nitrogen in aquatic environments, modified for estuaries (Aston, 1980) is shown in Fig.4.1.1.

4.1.2. Distribution of Nitrogen fractions in the estuary

4.1.2.1. Urea-N

Distribution of urea-N in the estuary during different seasons of the year are shown in Fig.4.1.2. It shows a steady decreasing trend from monsoon through post monsoon to pre monsoon. Higher values were observed near the river mouth and the lowest values observed were at a distance of 10Km from the river mouth (section 3) during all seasons. Generally, surface waters were found to contain more urea than the bottom waters in the estuary during the monsoon and post monsoon seasons.

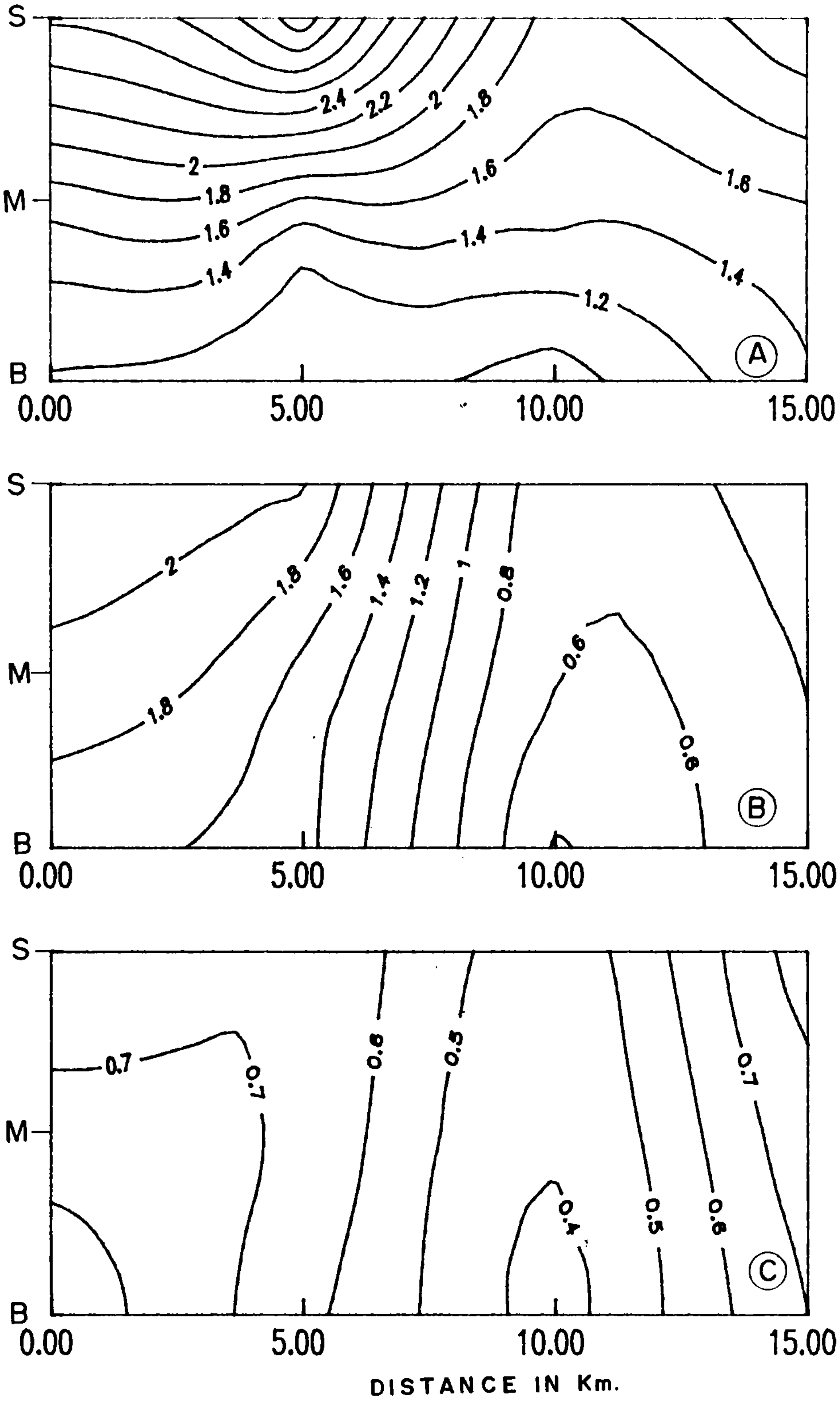


Fig. 4.1.2. Distribution of urea -N in the estuary during monsoon A, post monsoon B, pre monsoon C.

During the monsoon season, urea concentration ranged between 1.1 and 3.3 µgat/l in the lower sections (1 and 2) and between 0.9 and 2.2 µgat/l in the upper sections (3 and 4). Decrease in values were noticed during the post monsoon season, especially in the upstream sections where the observed values varied between 0.50 and 0.95 µgat/l. In the lower sections, the values ranged from 1.4 to 2.2 µgat/l. Urea concentration was found to be minimum during the pre monsoon season which recorded values ranging from 0.36 to 0.80 µgat/l and the distribution was almost uniform throughout the estuary except the low values (<0.5 µgat/l) at section 3.

4.1.2.2. Ammonia-N

Seasonal variations in the integrated mean values of ammonia concentration in the four sections of the estuary are shown in Fig.4.1.3. Ammonia concentration varied from non-detectable amounts during the premonsoon months at certain sections to a gradual build up during the monsoon months and high concentrations (> 5.0 µgat/l) during the post monsoon season. Isolated high concentrations (>15.0 µgat/l) were noticed in the month of January in the two upstream sections. Otherwise the ammonia concentration decreased gradually to lower values in the months of February to May. Monthly vertical profiles for ammonia distribution during the period of study are shown in Fig.4.1.5.

High ammonia concentrations with very little spatial variations (9.0 to 11.0 µgat/l) were observed during October. The mean values ranged between 4.0 and 7.0 µgat/l during November with higher values in the bottom waters at section 2. During December, higher concentrations were found at the river mouth section (5.0 to 7.0 µgat/l) and lower values (2.5 to 4.0 µgat/l) towards upstream. The lowest value (<1.0 µgat/l) observed was in the bottom waters at section 2. Very high ammonia concentration (18.0 to 20.0 µgat/l) in the uppermost section decreasing gradually to 3.0 µgat/l at the river mouth section was noticeable during January. The water column was vertically homogenous except in the upper estuary where slightly higher values were encountered at mid-depth.

Ammonia concentration decreased during February and March, and the values ranged between 0.4 and 1.4 µgat/l during February and <1.0 µgat/l during March. During both these months the minimum values were observed at section 2. During April and May, the vertical profiles showed an increase in the ammonia concentration towards the bottom of section 2.

In June, ammonia concentration decreased from a mean value of 2.8 µgat/l at the river mouth to 1.4 µgat/l at section 4. Much less spatial variations were observed during July when ammonia concentration was around 3.5 µgat/l in the estuary. A decrease in concentration (<2.0 µgat/l) was noticed towards upstream during August and September, while it was greater than 3.0 µgat/l at the river mouth with higher values in the bottom waters.

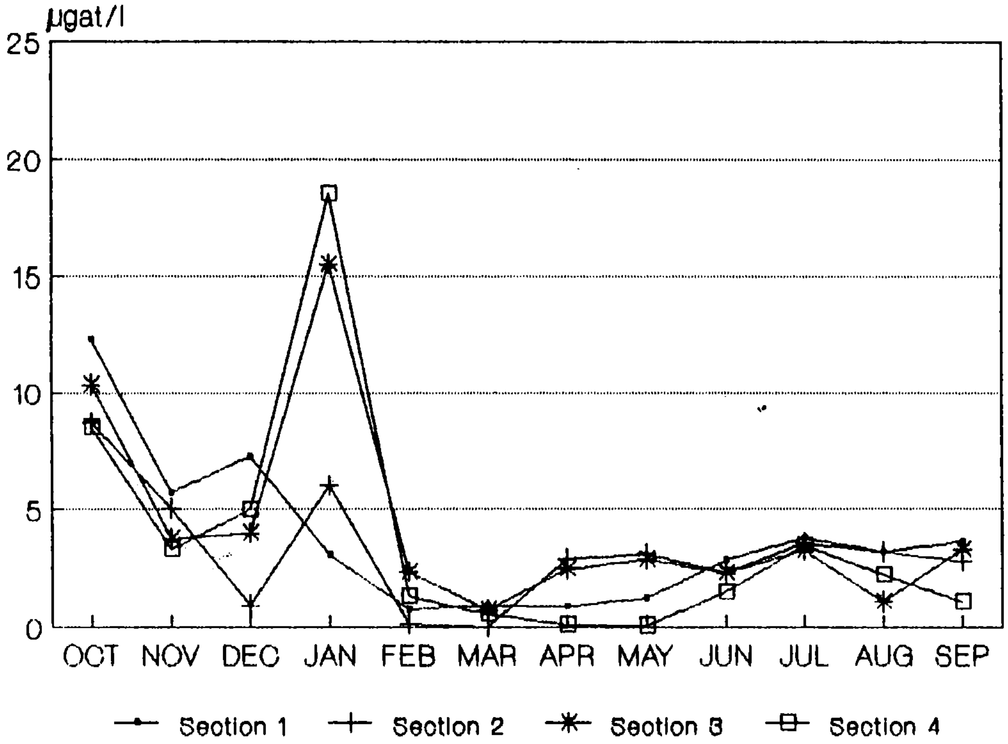


Fig.4.1.3. Seasonal changes of the integrated mean concentration of ammonia-N at four sections in the estuary.

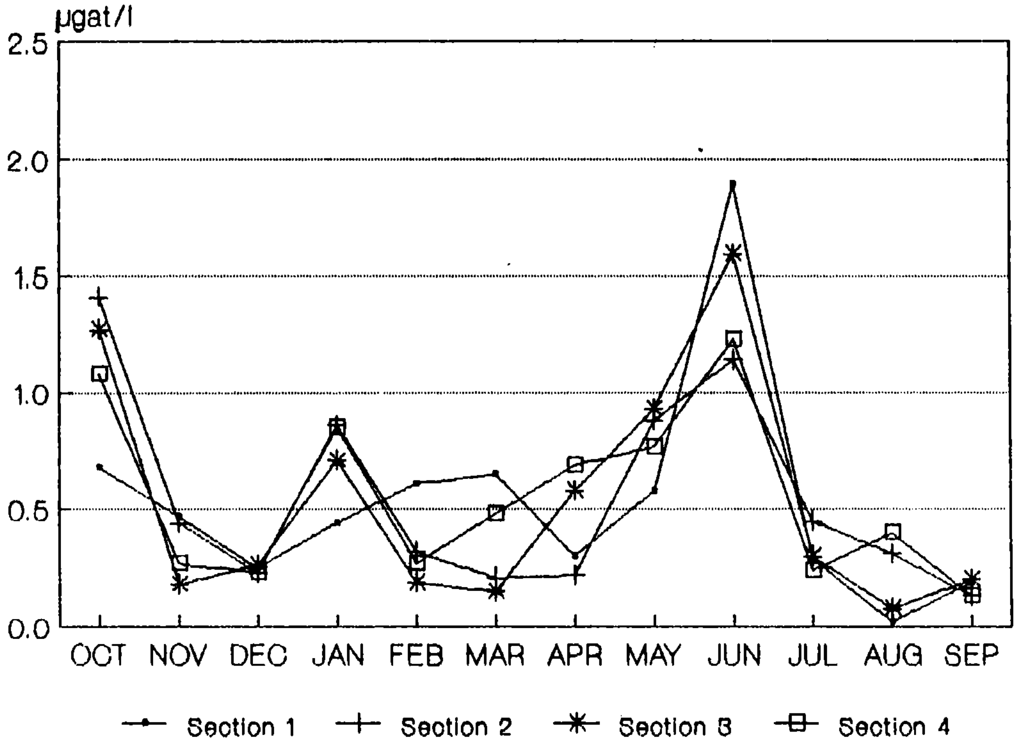


Fig.4.1.4. Seasonal changes of the integrated mean concentration of nitrite-N at four sections in the estuary.

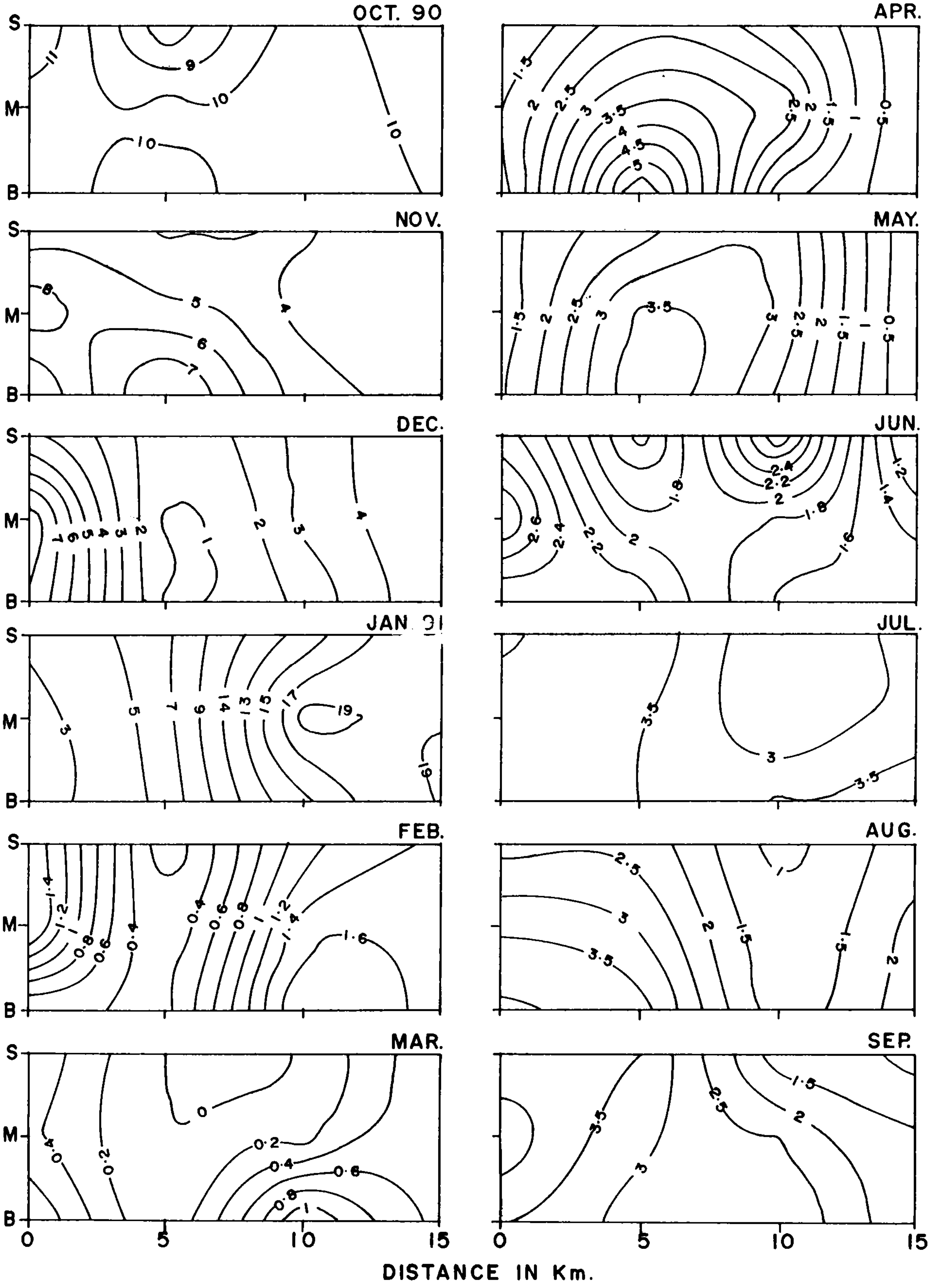


Fig. 4.1.5. Vertical profiles of NH_4^+ distribution in the estuary.

4.1.2.3. Nitrite-N

Seasonal changes in the integrated mean values of nitrite concentration are shown in Fig.4.1.4. Nitrite distribution did not followed a clear definite pattern. Very low concentrations (<1µgat/l) were observed throughout the estuary during the period of study with a few exceptions. The maximum value observed (1.9 µgat/l) was at the river mouth during June. A second maximum was observed during October at section 2. The vertical profiles (Fig.4.1.6) indicated that nitrite-N was distributed almost uniformly in the water column with greater horizontal variations.

During October, nitrite concentration increased from 0.7 µgat/l at the river mouth to 1.3 µgat/l at the section 5Km upstream and thereafter it remained more or less same in the upper estuary. The values ranged between 0.5 and 0.2 µgat/l during November with higher values at the marine end. Almost uniform concentration (0.25 µgat/l) was observed throughout the estuary during December. A gradual increase in nitrite concentration was observed from the river mouth towards upstream up to a distance of 5Km (values ranging from 0.4 to 0.8 µgat/l) and thereafter no such variation was noticed during January.

During February, nitrite concentration decreased gradually from 0.6 µgat/l at the river mouth to 0.2 µgat/l towards a distance of 10Km upstream and remained steady towards upstream. The vertical profiles showed a gradual

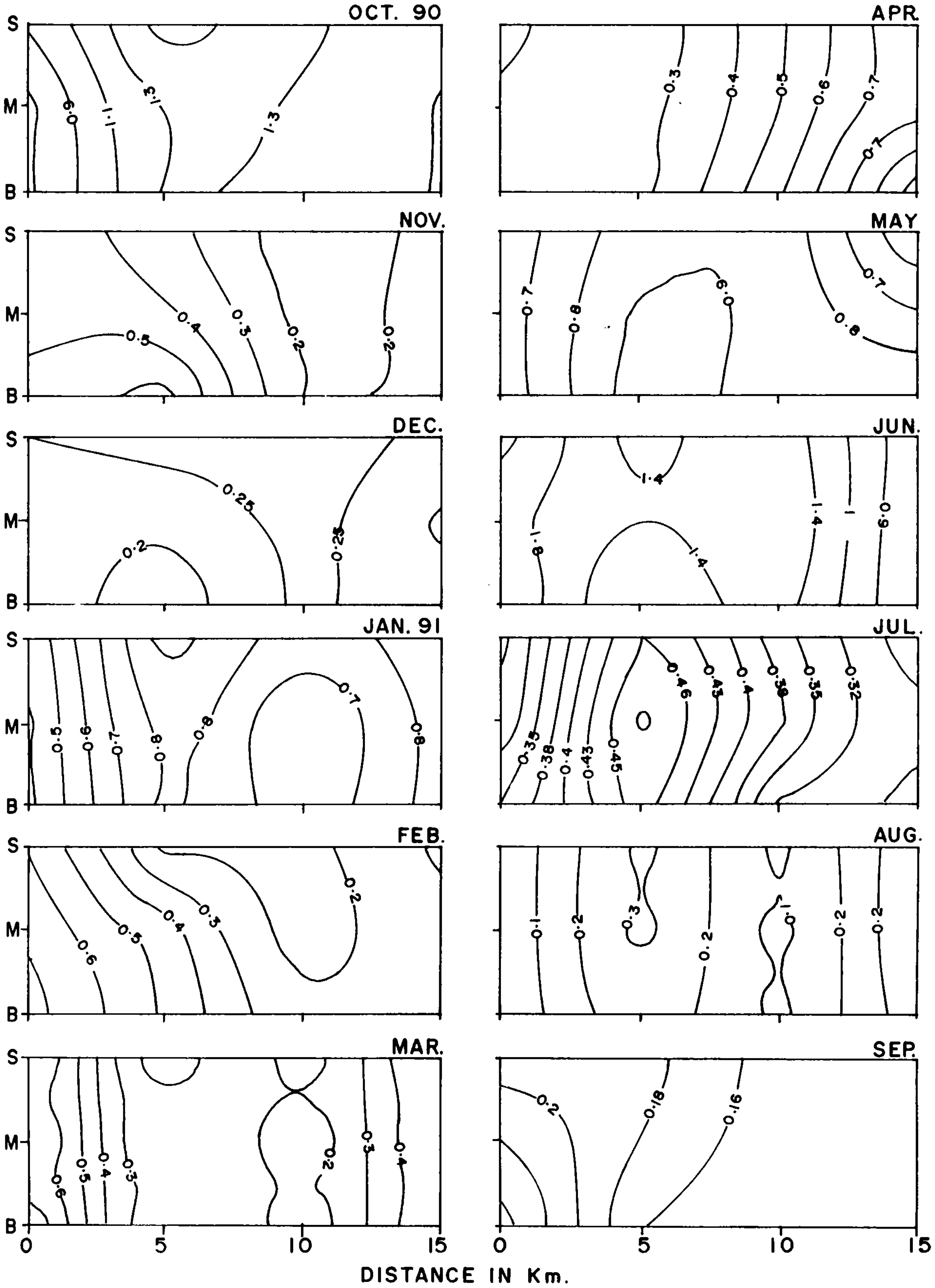


Fig. 4.1.6. Vertical profiles of nitrite distribution in the estuary

increase from the surface to bottom during this period. The situation was similar during March in the river mouth and the water column was vertically homogenous with respect to nitrite. There was a steady decrease in nitrite concentration from 0.6 µgat/l at the river mouth to 0.2 µgat/l at 5Km upstream. The low values were observed upto 10Km from the river mouth and thereafter it increased to 0.45 µgat/l at Section 4. During April, very low values (<0.3 µgat/l) were observed in the lower sections increasing gradually to 0.8 µgat/l at section 4. The average values observed during May ranged between 0.7 and 0.9 µgat/l in the estuary with the higher values at sections 2 and 3.

Nitrite concentration increased to 1.9 µgat/l, the maximum value encountered in the present study, during June. The high values were observed in the river mouth, which decreased to 1.4 µgat/l at sections 2 and 3, and then it decreased to 0.8 µgat/l in the upstream region. Nitrite was very low during July (0.2 - 0.4 µgat/l) with higher values around section 2. A further decrease in concentration was noticed during August with values ranging from 0.1 to 0.3 µgat/l and a uniform concentration around 0.15 µgat/l was observed during September.

4.1.2.4. Nitrate-N

Seasonal changes in the integrated mean concentration of nitrate at four sections in the estuary are shown in Fig.4.1.7. The annual cycle showed minimum nitrate

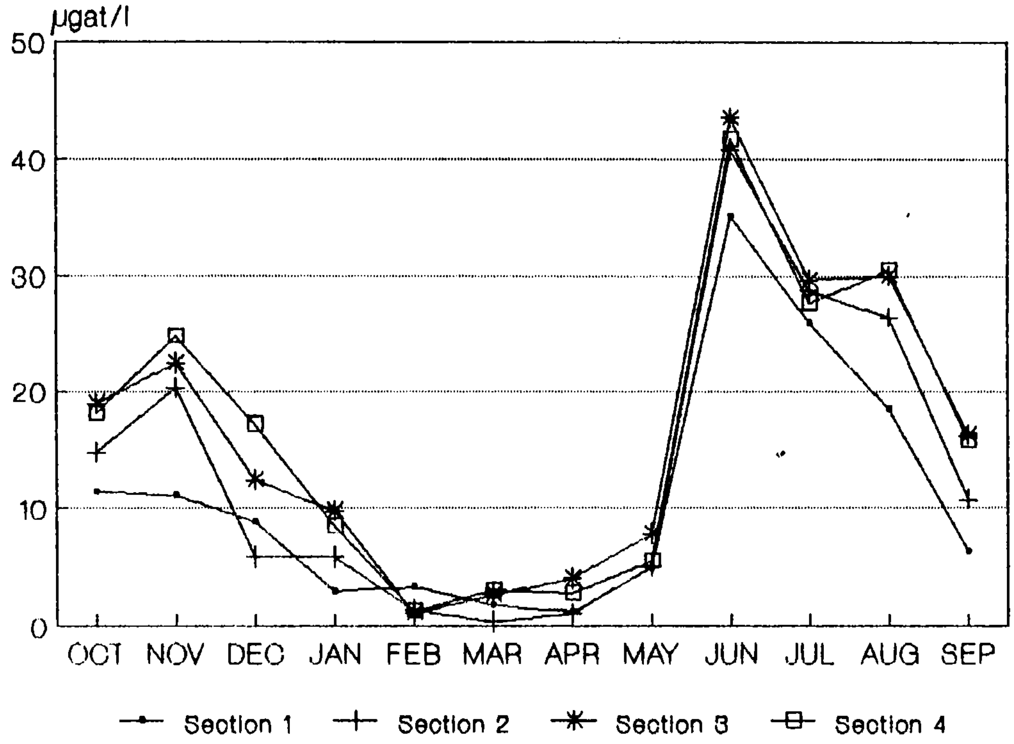


Fig.4.1.7. Seasonal changes of the integrated mean concentration of nitrate-N at four sections in the estuary.

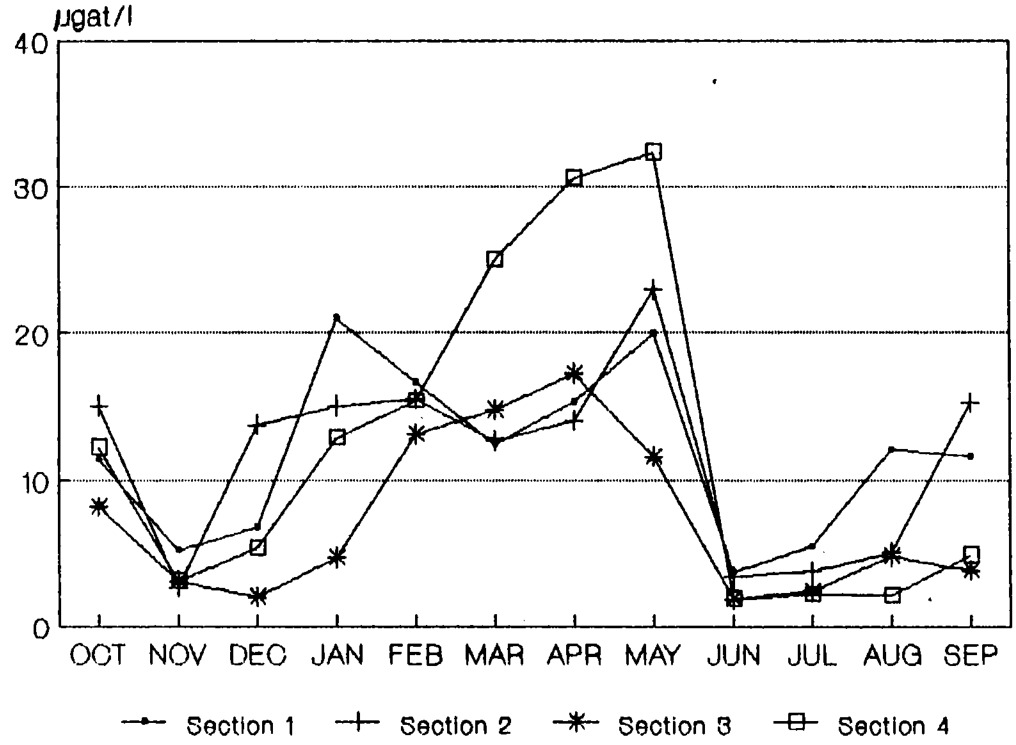


Fig.4.1.8. Seasonal changes of the integrated mean concentration of organic nitrogen at four sections in the estuary.

concentrations at all sections during the premonsoon followed by high concentrations during the monsoon and a decrease in levels during the post monsoon. The vertical profiles for nitrate distribution in the estuary during each month of observation are shown in Fig.4.1.9.

Analysis of spatial variation of nitrate during the period of observation revealed the following. During October, nitrate concentration showed a gradual increase from a mean value of 11 µgat/l at the river mouth section to 18 µgat/l at the section 15Km upstream. An increase in nitrate concentration with a similar trend in spatial variation was observed during November. Higher vertical variations were observed in the lower 10Km of the estuary during both these months. Values for the bottom waters were more variable in space compared to the surface. Spatial variations were negligible in the upper 10-15 Km segment of the estuary.

Nitrate concentration decreased during December and the spatial variations were negligible. On moving from the river mouth towards upstream, nitrate concentration increased from 9 µgat/l to 15 µgat/l at the surface and from 7 µgat/l to 13 µgat/l at the bottom. Lower values (<5.0 µgat/l) were observed at the bottom in the 5Km section (Section 2) of the estuary. During January, the decreasing trend continued and the vertical profiles showed a vertically homogenous water column with respect to nitrate in the lower estuary. Upstream sections showed greater spatial variations. The mean values ranged between 3.0 and 10.0 µgat/l in the estuary.

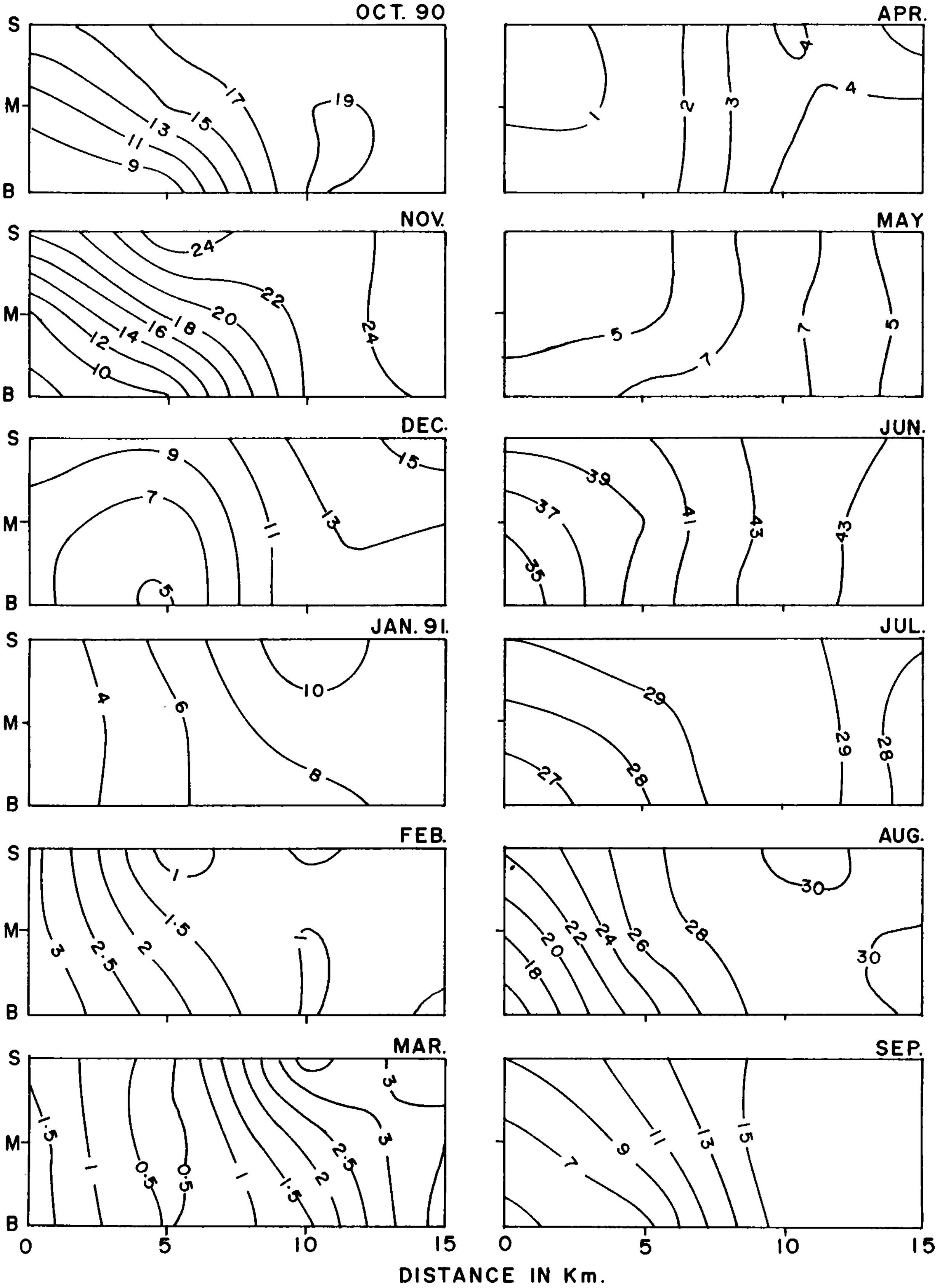


Fig. 4.1.9. Vertical profiles of Nitrate distribution in the estuary.

Nitrate concentration decreased to a minimum value during February and a reverse trend in the spatial variation was noticeable. Higher values were observed towards the bottom in the marine end (2.5 - 3.5 µgat/l) and very low values (< 1.0 µgat/l) in the upstream sections. During March, nitrate distribution showed higher values in the upstream region compared to downstream. The lowest concentration observed were around section 2 (<0.5 µgat/l). A gradual increase from a mean value of 1.0 µgat/l at the rivermouth to 4.0 µgat/l at the upstream section was noticeable during April. Nitrate concentration increased throughout the estuary during May (mean values of 5.0 to 7.0 µgat/l) and the higher values observed were in the 5-10 Km region of the estuary.

With the onset of monsoon in the month of June, nitrate concentration increased drastically. The maximum value observed was a uniform concentration of 43.0 µgat/l in the water column at section 4 which decreased to 39.0 µgat/l at the surface and 34.0 µgat/l at the bottom of section 1. Vertical gradients of 2.0 - 5.0 µgat/l were observed upto 5 Km from the river mouth and beyond that the water column was vertically homogenous. Nitrate concentration decreased during July and August with very little spatial variations in July (27.0 - 29.0 µgat/l) and greater variations during August (18.0 - 30.0 µgat/l). A further decrease with higher stratification was observed during September and the mean values ranged between 6.5 and 15.0 µgat/l. No spatial variation in nitrate concentration was observed beyond a distance of 10 Km from the mouth during August and September.

4.1.2.5. Organic-N

Seasonal variation in the integrated mean values of organic nitrogen in the estuarine waters (Fig.4.1.8) showed an inverse trend with that of nitrate-N. Spatial distribution of organic-N for each month is shown in the vertical profiles (Fig.4.1.10).

During October, organic-N was high in the lower part of the estuary and the maximum concentration (17.0 µgat/l) was observed at the bottom of section 2. A gradual, decrease was noticed towards the surface. But in the upstream sections, organic-N decreased from the surface to bottom with a minimum concentration (< 7.0 µgat/l) at section 3. Organic-N concentration decreased during November, which showed values ranging from 3.0 to 6.0 µgat/l throughout the estuary. Comparatively higher values were observed at section 1, where nitrate concentrations were minimum. Considerable increase in organic-N was observed in the lower part of the estuary during December. The maximum concentration of organic-N at section 2 coincided with the nitrate minimum. A gradual decrease from the river mouth towards upstream and a minimum value at section 3 was noticed during January. Organic nitrogen concentrations as high as 21 µgat/l was observed at section 1 and <6.0 µgat/l at section 3.

Organic nitrogen increased during February except at section 1 and the distribution was almost uniform throughout

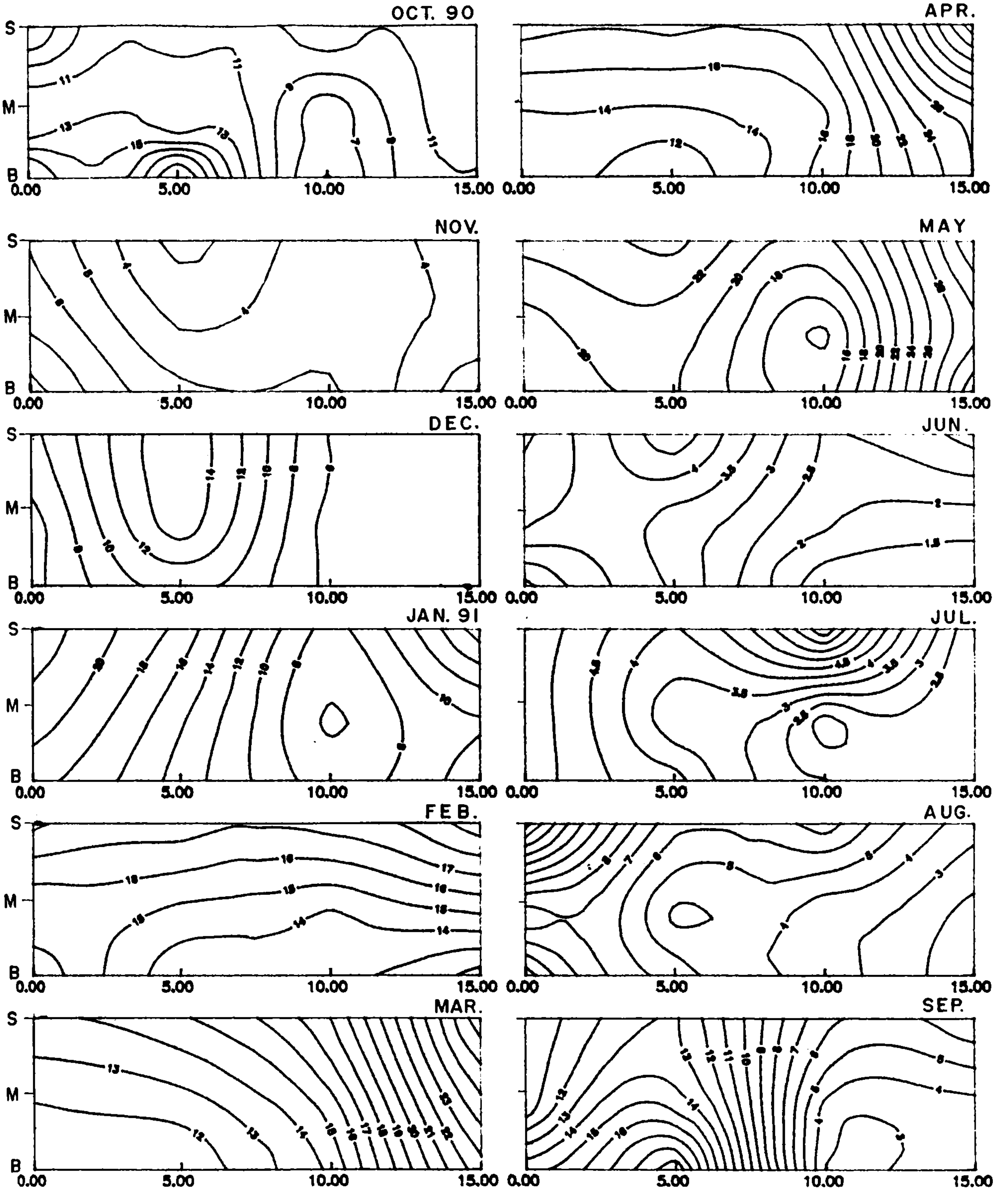


Fig. 4.1.10. Vertical profiles showing the distribution of organic nitrogen in the estuary.

the estuary. The distribution of organic-N from March to May followed the same pattern with lower values (12-20 µgat/l) at sections 1-3 and exceptionally high values (>30 µgat/l) at section 4. Generally surface values were found to be higher than that of the bottom.

Concentration of organic-N sharply decreased to very low values during June (1.5 to 4.0 µgat/l) and July (2.0 to 5.0 µgat/l) throughout the estuary. During August, an increase in concentration (>10 µgat/l) was observed at section 1 and it was maximum (18 µgat/l) at the bottom of section 2 during September.

4.1.3. Tidal variations of nitrogen fractions

Tidal variations of various nitrogen fractions are analysed to investigate the extent to which tides affected these parameters during different seasons. Influence of tide during monsoon was limited to section 1 only and wide variations in concentrations were observed for various nitrogen fractions during a tidal cycle (Fig 3.2.6). Ammonia-N showed opposing trend with tide and it was minimum during flood tide. Nitrite concentration increased during flood tide and bottom values were higher throughout the tidal cycle. Nitrate-N was found to decrease during flood tide and slowly increased during the ebb period.

During the post monsoon season, nitrite concentration was found to increase with flood tide while a decrease in

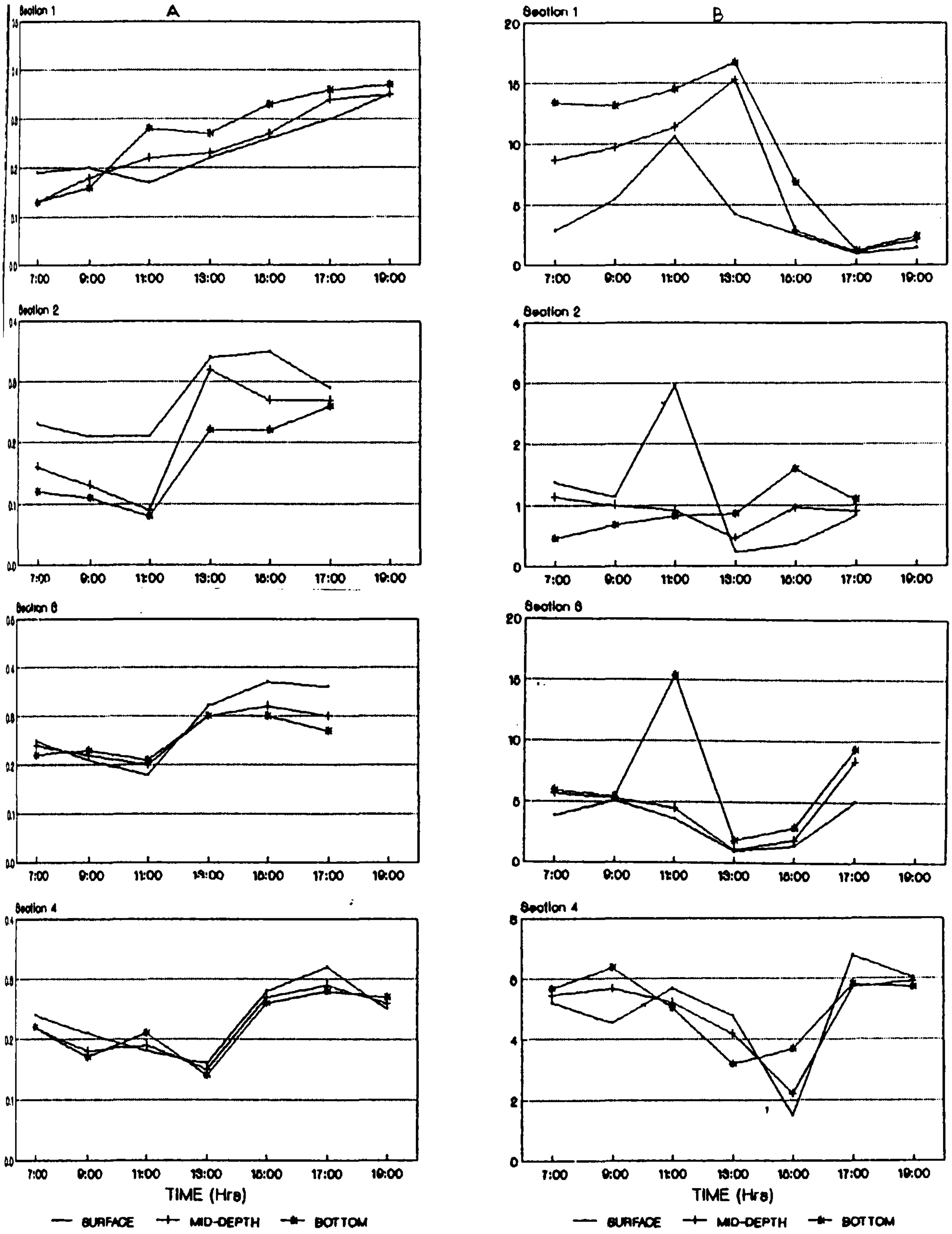


Fig.4.1.11. Tidal variations in nitrite-N (A) and ammonia-N (B) during post monsoon.

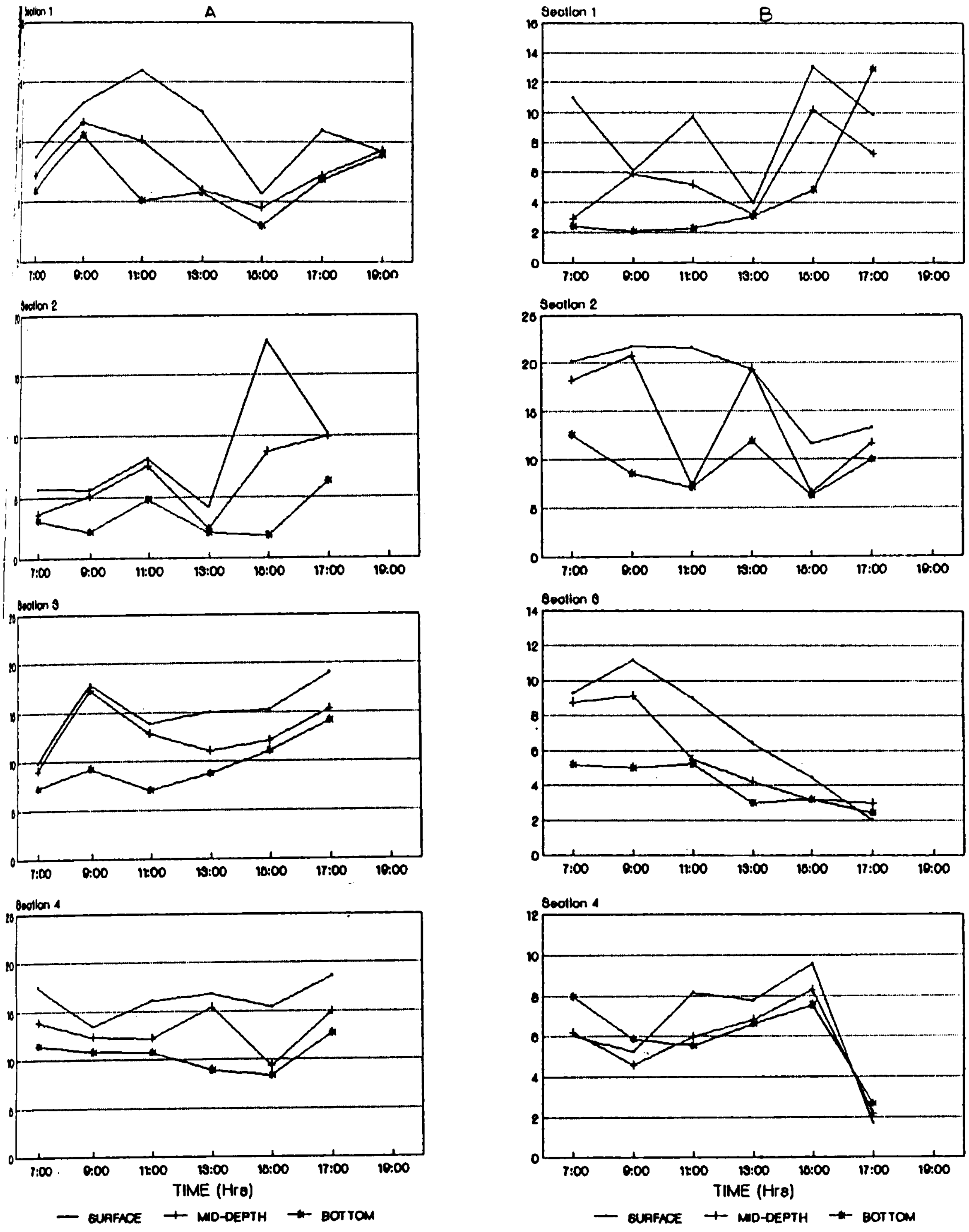


Fig.4.1.12. Tidal variations in nitrate-N (A) and organic-N (B) during post monsoon.

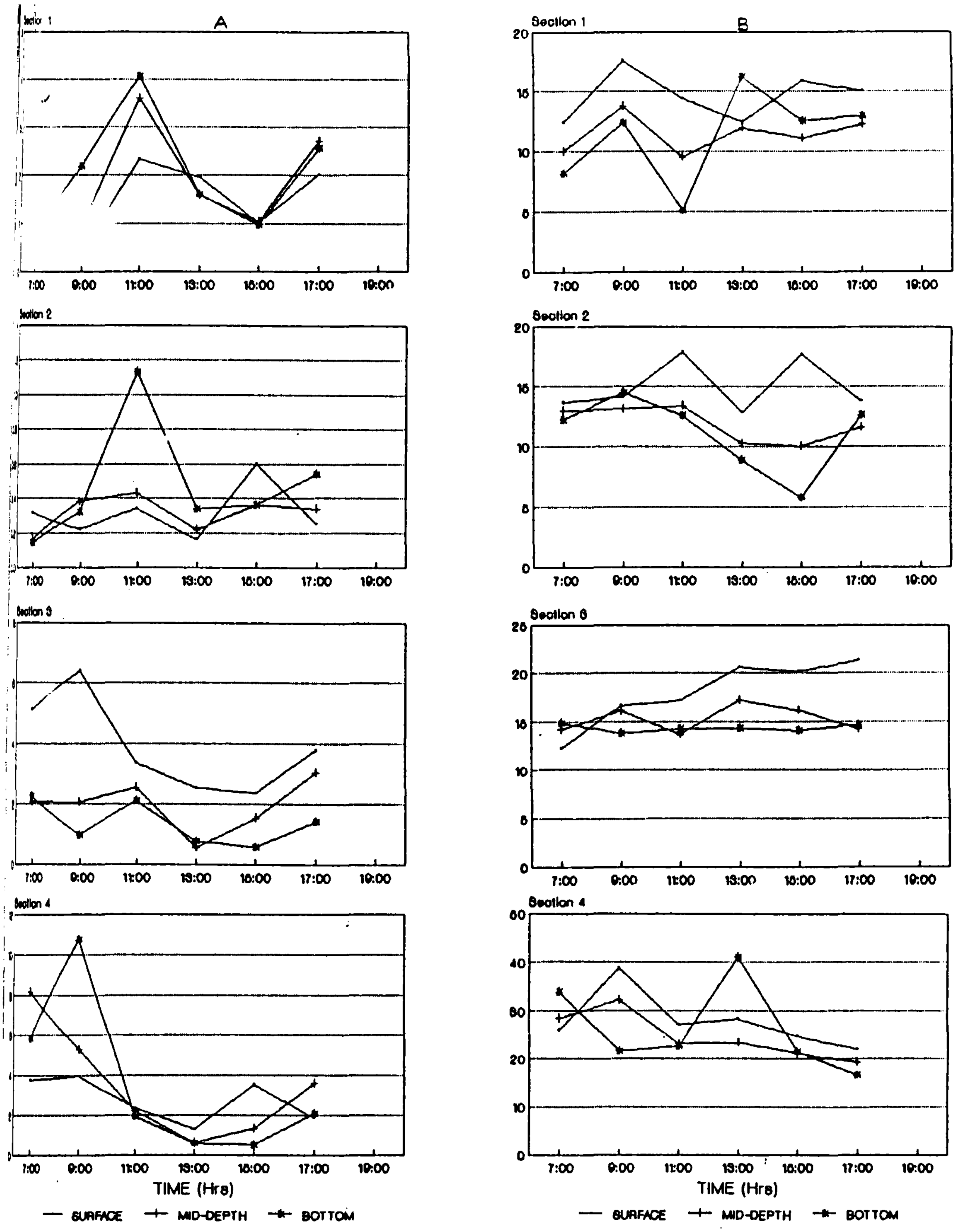


Fig.4.1.13. Tidal variations in nitrate-N (A) and organic-N (B) during pre monsoon.

ammonia-N was noticed at all sections except at section 1 (Fig 4.1.11). Ammonia concentration increased during the high water regime and then decreased while nitrite was found increasing even after the flood period. Generally, at all sections in the estuary, the nitrite peak follows an ammonia peak in a tidal cycle. Nitrate concentration decreased during flood tide and a clear inverse trend was observed with salinity distribution in the upstream sections (Fig 4.1.12). Organic nitrogen distribution followed the same pattern as that of salinity with the tide except at section 1.

During the pre monsoon season, nitrite and ammonia variations within a tidal cycle was very small throughout the estuary. Tidal variations of nitrate and organic nitrogen are shown in Fig 4.1.13. Nitrate concentration was found to be maximum at the bottom during flood tide at sections 1 and 2. A clear inverse relation with salinity was observed at sections 3 and 4. Organic nitrogen concentrations were found to be higher at the surface and no clear relation with salinity or tide was observed in the downstream sections. At sections 3 and 4 organic nitrogen distribution showed a clear relationship with salinity during the tidal cycle.

4.1.4. DISCUSSION

Seasonal distribution of various nitrogenous nutrients in the estuary was affected by physical, chemical and biological processes. The contribution of various nitrogen fractions to the total nitrogen pool of the estuarine waters was found to vary spatially and temporaly. The major source of inorganic nitrogen was through river discharge which was indicated by their maximum concentration during monsoon. During the pre monsoon months when the riverine contribution was very little, percentage of inorganic nitrogen in the estuarine waters was found to be the minimum and the major form of nitrogen was organic. During post monsoon season, the contribution of both these components were almost equal in the estuarine waters eventhough there existed a predominance of the inorganic form. Generally, dissolved nitrogen compounds are present throughout the estuary during all seasons of the year in one form or other and so nitrogen was not a limiting nutrient in the estuary.

A discussion of the seasonal variation in the distribution of various nitrogen fractions in the estuary will help in understanding the nutrient chemistry of the estuary. The degree to which phytoplankton nitrogen uptake processes affect estuarine nitrogen concentration varies between different estuarine systems (Mc Carthy, 1981). Several factors including external environmental conditions such as temperature, light, nutrient concentration and physiological state of the phytoplankton ultimately regulate the rate of nitrogen uptake in the estuary. The effect of these uptake processes on ambient nitrogen distributions are determined by the physical characteristics such as flushing rate and circulation in the estuary (Pennock, 1987). Tidal mixing of the water column appears to be one of the factors responsible for the differing responses of phytoplankton populations to nutrient inputs observed in estuaries (Monbet, 1992). Microbial transformations of nitrogen may be as important as phytoplankton uptake of inorganic nitrogen in determining the distributions of nitrogen among the major dissolved forms (Horrigan et al, 1990).

Percentage of different nitrogen fractions at various sections in the estuary is given in Table 4.1.1. Contribution of urea-N to the total-N pool of the estuary was found to be minimum during premonsoon (1.8 to 3.7 %). The contribution was maximum in the upstream sections during monsoon months (3.7 to 5.3 %) while it was maximum in the river mouth region during the post monsoon period (6.2 to 7.3%). Trends in the seasonal variation of urea observed in the Chaliyar river estuary was similar to that reported by Verlencar (1985) in the Mandovi estuary. The concentration was highest during the monsoon when physical processes like precipitation and land drainage were active. A slight decrease in concentration was observed after the south-west monsoon because of the decrease in land drainage. Urea-N in the estuary decreased to minimum values during the premonsoon season and this may be due to the utilization by phytoplankton during this period. A high phytoplankton population was also observed during these months (S. Kumaran, personal communication). Utilisation and decomposition of urea associated with phytoplankton activity have been reported by several workers (Carpenter et al., 1972; Mitamura and Saijo, 1980; Verlencar, 1985).

Table 4.1.1. Percentage of different nitrogen fractions at various sections in the Chaliyar River Estuary.

Sections	Percentage			
	Nitrite + nitrate	Ammonia-N	Urea-N	Organic-N
PRE MONSOON				
S-1	13.80	4.80	3.70	77.70
S-2	10.60	7.60	3.30	78.50
S-3	18.80	9.80	1.80	69.60
S-4	10.00	1.50	2.60	85.90
MONSOON				
S-1	65.90	10.00	5.70	18.40
S-2	72.30	8.20	6.10	13.40
S-3	85.00	7.10	3.70	4.20
S-4	85.70	6.10	5.30	2.90
POST MONSOON				
S-1	32.00	27.20	7.30	33.50
S-2	38.60	18.60	6.20	36.60
S-3	54.40	28.90	1.70	15.00
S-4	48.80	26.60	2.60	22.00

Occurrence of urea in significant quantities in the estuarine waters indicate the important contribution of this compound to regenerated production. Mc Carthy and Eppley (1972) using phytoplankton cultures found that ammonia at elevated concentrations could be used in preference to urea, urea-N and nitrate are being utilised simultaneously over a wide range of concentrations. Mc Carthy et al.(1977) found high preference in phytoplankton for ammonia and urea over nitrate and nitrite.

Contribution of ammonia to the total nitrogen pool of the estuary was <10% during the monsoon and premonsoon periods. Maximum accumulation of ammonia (>25% of total N) occurred during the postmonsoon period when the opposing forces, viz. river runoff and tidal incursion were moderate. Ammonia-N did not constitute a major component in the river water; therefore its concentration is subjected to little influence by river discharge. Ammonia distribution in the water column clearly indicated the process of ammonification in the estuarine and riverine part, which is the ultimate step in the autoepuration of organic matter. Added to this also the transfer of ammonia from the interstitial water in the bottom sediments which was rich in ammonia (Table 4.4.3).

An examination of ammonia data in the interstitial water at various sections during different seasons (Table 4.4.3) indicated that it is minimum during the post monsoon season and the values are lowest at sections 3 and 4. But the ammonia concentrations are uniformly high in the water column with maximum values at the upstream sections. The transfer of ammonia to the overlying water can only be minimal at sections 3 and 4 where the interstitial water values are low. Therefore it strengthens the argument that the high amount of ammonia encountered can only be due to ammonification in the water column.

Nitrite concentration was found to be significantly high only during the postmonsoon season. A close look at the tidal variations during this period showed the sequence of a peak concentration of ammonium followed by an increase in nitrite at all sections. This was indicative of nitrification in the water column as reported by several workers like Ward and Twilley (1986) and Fan and Jin (1989). Here nitrifying bacteria can play an important role because they are able to oxidise ammonium to nitrate with nitrite as an intermediate. Nitrite may also be formed in the reduction of nitrate and denitrification.

Heavy rainfall and consequent land drainage was observed to be the main source of nitrate in the estuary. High nitrate concentration in the run-off waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Nitrates are not well retained by the soil and if not utilised quickly are leached away along with land drainage. Since nitrates are highly water-soluble, most of it may be leached away during the initial runoff period and this could be the reason for the decrease in nitrate concentration during July and August eventhough the river discharge was high. A second nitrate peak observed during November is due to the influence of river runoff during the north-east monsoon. A gradual decrease in concentration was observed downstream and the fluctuations observed at the barmouth section was according to the phase of the tide. Much of the nitrate was washed out of the estuary during the period of high runoff without being assimilated, due to short residence time and slow uptake rate of nitrate by phytoplankton.

Nitrate concentration decreased during December and January due to the decrease in contribution from the land source and increased uptake by primary producers. During the premonsoon months from February to May, the entire estuary was marine dominated and the contribution of nitrate from fresh water was practically absent. This together with the high biological activity brought nitrate concentration to a minimum. But during this period, there was an increase in organic-N concentration. The reduction in the inorganic nitrogen accompanied by a substantial increase in the percentage of organic-N indicated that the major source of organic-N in this system is not the river runoff.

During the monsoon period, when land drainage and river discharge were maximum, 80-90% of the total nitrogen pool in the estuary was contributed by nitrate alone. On the other hand during the premonsoon period, when the estuary was marine dominated, 75-85% of the total nitrogen pool was organic-N. Generally an inverse relationship was observed

Table 4.1.2. Percentage of inorganic and organic nitrogen fractrions in the Chaliyar river estuary and Mandovi- Zuari estuarine system, based on average values of all the stations.

	Chaliyar		Zuari[*]		Mandovi[*]	
	Inorganic	Organic	Inorganic	Organic	Inorganic	Organic
JAN	54.5	45.5	29.0	71.0	38.0	62.0
FEB	19.5	80.5	62.0	38.0	71.0	29.0
MAR	13.9	86.1	20.0	80.0	19.0	81.0
APR	19.2	80.8	18.0	82.0	14.0	86.0
MAY	28.9	71.1	21.0	79.0	26.0	74.0
JUN	93.9	6.1	82.0	18.0	83.0	17.0
JUL	80.4	19.6	61.0	39.0	62.0	38.0
AUG	82.4	17.6	48.0	52.0	53.0	47.0
SEP	63.4	36.6	24.0	76.0	29.0	71.0
OCT	67.9	32.1	50.0	50.0	62.0	38.0
NOV	86.5	13.5	50.0	50.0	69.0	31.0
DEC	67.9	32.1	53.0	47.0	24.0	76.0

[*] Qasim and Sen Gupta, 1981.

between the inorganic and organic forms of nitrogen in the estuary, Such an inverse relationship has been reported in the waters of western English Channel (Butler et al., 1979). A sharp rise in organic-N accompanied by a depletion of inorganic nitrogen during pre and post monsoon seasons is indicative of phytoplankton productivity and nutrient enrichment due to favourable physicochemical conditions.

The general trend in the seasonal variation of inorganic and organic nitrogen fractions in this system (Table 4.1.2) is well comparable with that of Mandovi-Zuari estuarine system (Qasim and Sen Gupta, 1981).

4.2. THE PHOSPHORUS CYCLE

Phosphorus predominantly occurs in nature in the +5 Oxidation state as the orthophosphate group PO_4^{3-}, bound to a cation in insoluble inorganic compounds or as a component of organic molecules. Typical inorganic compounds are the apatites - $Ca_{10}(PO_4)_6(F,OH)_2$, Calcium phosphate - $Ca_3(PO_4)_2$, aluminium phosphate - $AlPO_4$, and iron(iii)phosphate - $FePO_4$. Phosphorus is an essential constituent of the energy transferring molecules ATP, ADP and AMP, and of the genetic information carrying molecules DNA and RNA. This means that phosphorus is an essential element for all living organisms and it is often a limiting factor in the fertility of soils and aquatic ecosystems. The low solubility of the inorganic compounds limits its availability as a nutrient.

4.2.1. Phosphorus in the Aquatic Environment

Ecological interest in phosphorus stems from its major role in biological metabolism and the relatively small amounts of phosphorus in the hydrosphere. The weathering of the earth's crust and surface water transport deliver phosphorus to estuaries as phosphate minerals in suspended detritus and dissolved phosphate in river water. The supply of phosphorus to water bodies depends to a large extent on the solubility of phosphorus found in sediments and in suspended inorganic particles (Avnimelech, 1983). Also, phosphorus is contributed to estuaries from domestic sewage and industrial effluent disposal into rivers and from tidal waters. The general phosphorus cycle describing the various sources and sinks modified for estuaries (Aston, 1980) is shown in (Fig.4.2.1).

The mechanism of cycling of phosphorus as a nutrient to the growth of phytoplankton and zooplankton depends on a complex set of biologically mediated reactions. Phytoplankton normally satisfy their requirements of phosphorus by direct assimilation of orthophosphate (Riley and Chester, 1971). The average composition of phytoplankton can be roughly designated by the empirical formula $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$, and the oxidative regeneration of nitrate and phosphate from it can be represented by the equation

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\ O_2 \longrightarrow 106\ CO_2 + 122\ H_2O + 16\ NO_3^- + PO_4^{---} + 19\ H^+$$

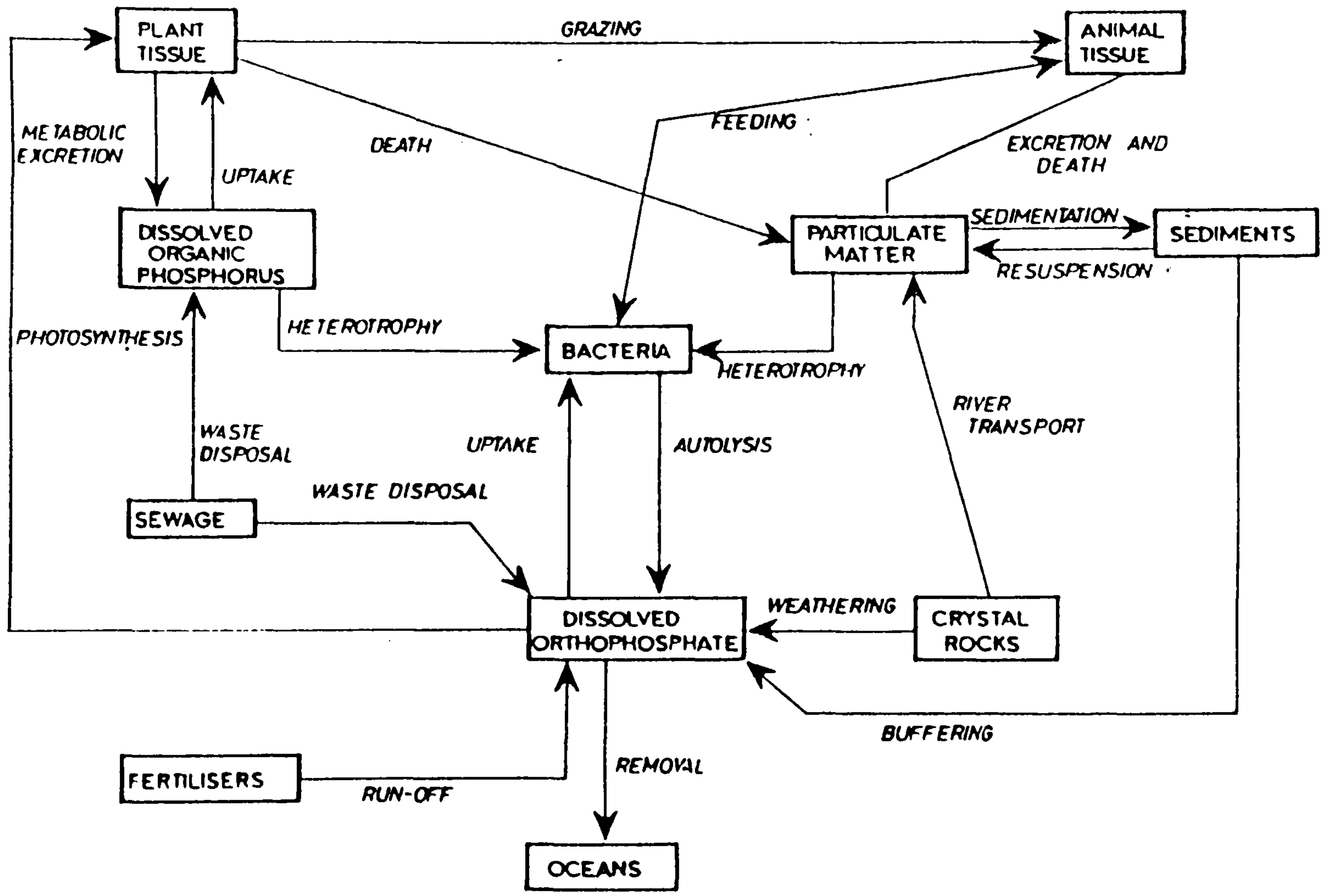


Fig.4.2.1. Phosphorus cycle in the estuarine environment.

In seawater at pH around 8.0, the predominant dissolved inorganic species is HPO_4^{--} (87%). The remaining as PO_4^{---} (12%) and $H_2PO_4^-$ (1%). Though the polyphosphates were not found in seawater, it may present in estuarine and coastal waters as a result of pollution from detergents (Koroleff[4], 1983).

The availability of phosphorus in natural systems significantly affects biological production. In many aquatic systems, the rate of primary production and the accumulation of phytoplankton biomass are influenced by the concentration and flux of phosphorus (Jaworski, 1981; Schindler, 1985). In estuaries, the rate of phosphorus recycling has been found to vary considerably with turnover time of PO_4^{3-} ranging from minutes (Taft et al., 1975) to days (Friebel et al., 1978; Berman, 1983).

In coastal waters, the interaction between the water column and the sediment can have a large influence on phosphorus concentration and the overall productivity of the ecosystem (Jitts, 1958; Pomeroy et al., 1965; Nixon, 1981). In regions of high productivity, sediments are often rich in biogenic debris, especially essential plant nutrients such as N and P compounds (Suess, 1981). Sediments can act either as a source or as a sink of phosphorus by adsorption-desorption reactions and therefore buffer the phosphorus concentration in the water column (Carritt and Goodgal, 1954; Pomeroy et al., 1965; Buttler and Tibbitts, 1972; Strom and Biggs,1982). Thus the phosphorus composition of coastal and estuarine sediments is intimately linked to the phosphorus concentration in the water column and the fluxes of biogenic material in the sediment.

Reddy and Sankaranarayanan (1972) have reported the probable factors influencing the regenerative capacity of sediments of Cochin estuary. The difference in the regenerative property of the sediments were attributed to the large variations of nutrient concentrations in the overlying waters. The distribution of various forms of phosphorus in the sediments of Cochin estuary during different seasons and its exchange between the sediment and the overlying waters in relation to the texture of of the sediments had been studied by several workers (Murty and Veerayya, 1972; Ansari and Rajagopal, 1974; Nair et al., 1993). Fine sediments of silt and clay showed higher content of phosphorus than coarse sandy sediments.

4.2.2. Distribution of phosphorus in the estuary

4.2.2.1. Dissolved inorganic phosphate

Seasonal variation in the integrated mean concentration of phosphate is shown in Fig 4.2.3. The seasonal trends observed in the phosphate distribution were less marked compared to the nitrate distribution. Phosphate concentrations were relatively low (<1.0 µgat/l) throughout the estuary with a few exceptions. The peak values observed were at the upstream sections during Dec-Jan. The peak value

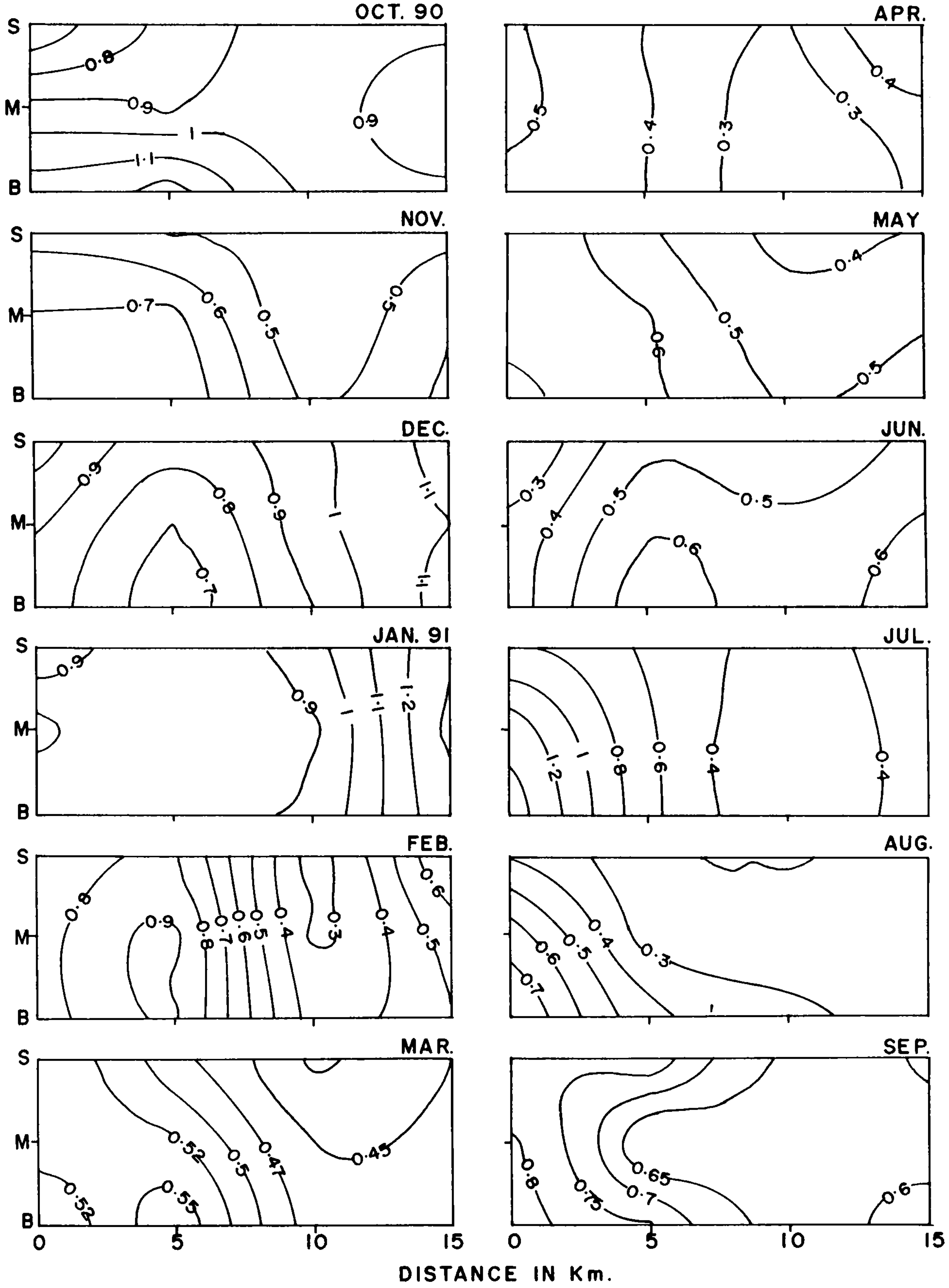


Fig. 4.2.2. Vertical profiles of Phosphate distribution in the estuary.

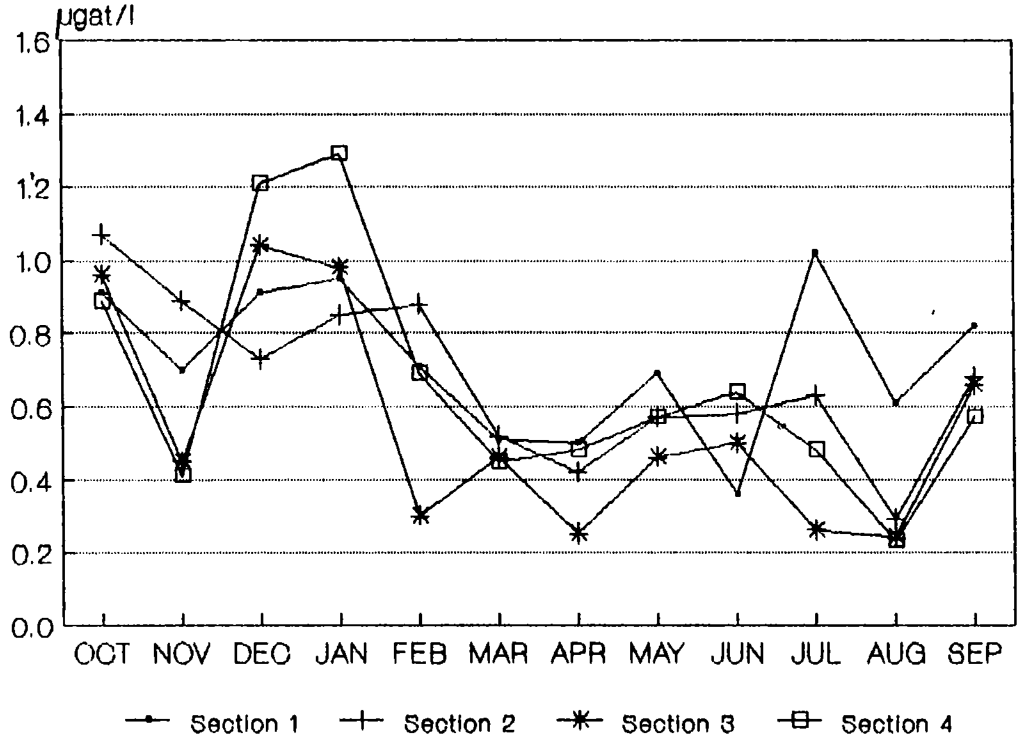


Fig.4.2.3. Seasonal changes of the integrated mean concentration of inorganic phosphate at four sections in the estuary.

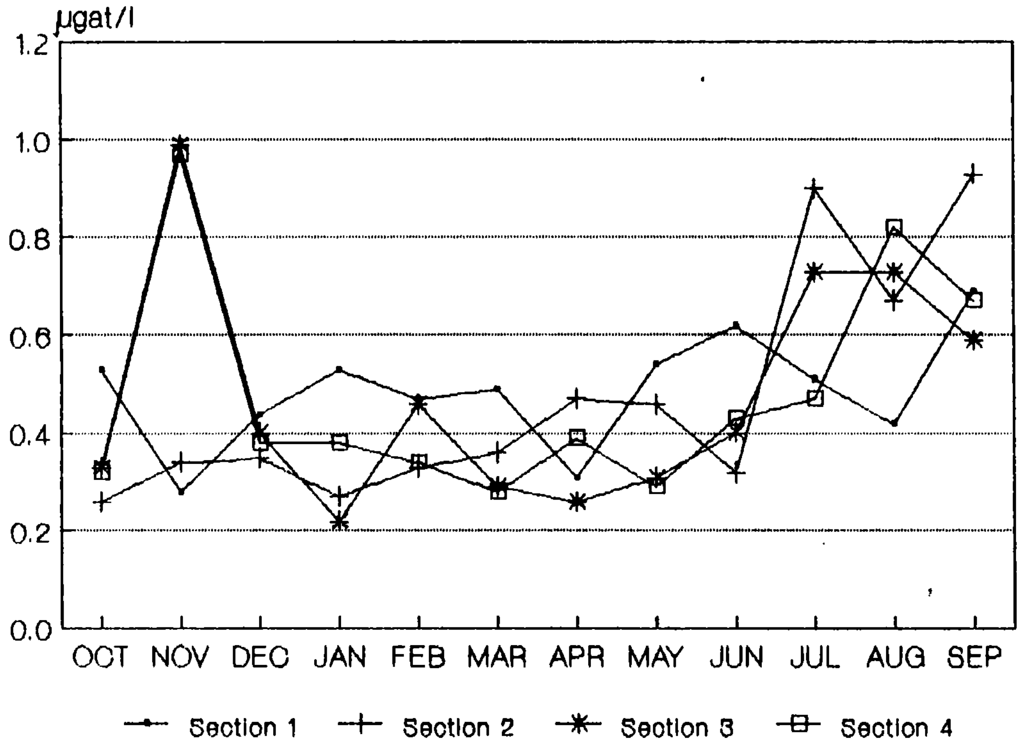


Fig.4.2.4. Seasonal changes of the integrated mean concentration of organic phosphorus at four sections in the estuary.

noticed at the river mouth was during July.

Vertical profiles of phosphate distribution in the estuary for each month of observation during the present study are shown in Fig 4.2.2. Analysis of spatial variation of phosphate at sections 1 to 4 during different months revealed the following: During October, the surface to bottom variation observed was from 0.7 µgat/l to 1.1 µgat/l at section 1 and 0.8 to 1.2 µgat/l at section 2. Almost uniform concentration of about 0.9 µgat/l in the water column was observed at sections 3 and 4. A general decrease in phosphate concentration with very less horizontal or vertical variations and average values varying between 0.5 and 0.7 µgat/l were noticeable during November. During December, phosphate concentration increased from a mean value of 0.8 µgat/l at the river mouth to 1.1 µgat/l at section 4 in the surface waters. Lower values were observed in the bottom waters, especially around section 2 where a minimum value of 0.7 µgat/l was noticed. On moving along the axis of the estuary from the river mouth towards upstream, a gradual increase in phosphate concentration with very less vertical variations was observed during January. The values ranged between 0.78 and 1.25 µgat/l.

Phosphate concentration decreased during February and the lowest value observed was 0.30 µgat/l at section 3. The maximum value noticed was 0.90 µgat/l at the bottom of section 2. Values ranging between 0.45 and 0.55 µgat/l with very little vertical or horizontal variations were observed during March. April recorded the lowest phosphate concentration among the pre monsoon months. The minimum value observed was at section 3 which was 0.25 µgat/l in the water column and the maximum was 0.50 µgat/l at the river mouth surface waters. A similar trend with slightly increased values ranging between 0.40 and 0.65 µgat/l was observed during May.

Phosphate concentration remained more or less same during June when the estuary was fresh-water dominated. The mean values fluctuated between 0.38 to 0.62 µgat/l from sections 1 to 4. A peak value (>1.0 µgat/l) was observed at the river mouth during July and it decreased to 0.40 µgat/l in the upstream sections. At the river mouth section, pronounced vertical variations ranging from 0.80 µgat/l at the surface to 1.30 µgat/l at the bottom and the higher values during high tide were noticed. A vertically homogenous water column was observed in the upstream sections. Lower values with a similar trend in spatial distribution was observed during August. At the river mouth section, values increased from 0.40 µgat/l at the surface to 0.80 µgat/l at the bottom. Phosphate concentration decreased towards upstream with negligible vertical variations, and the mean value observed beyond 5Km from the river mouth was 0.30 µgat/l. During September, the values fluctuated between 0.60 and 0.80 µgat/l with no marked horizontal or vertical variations.

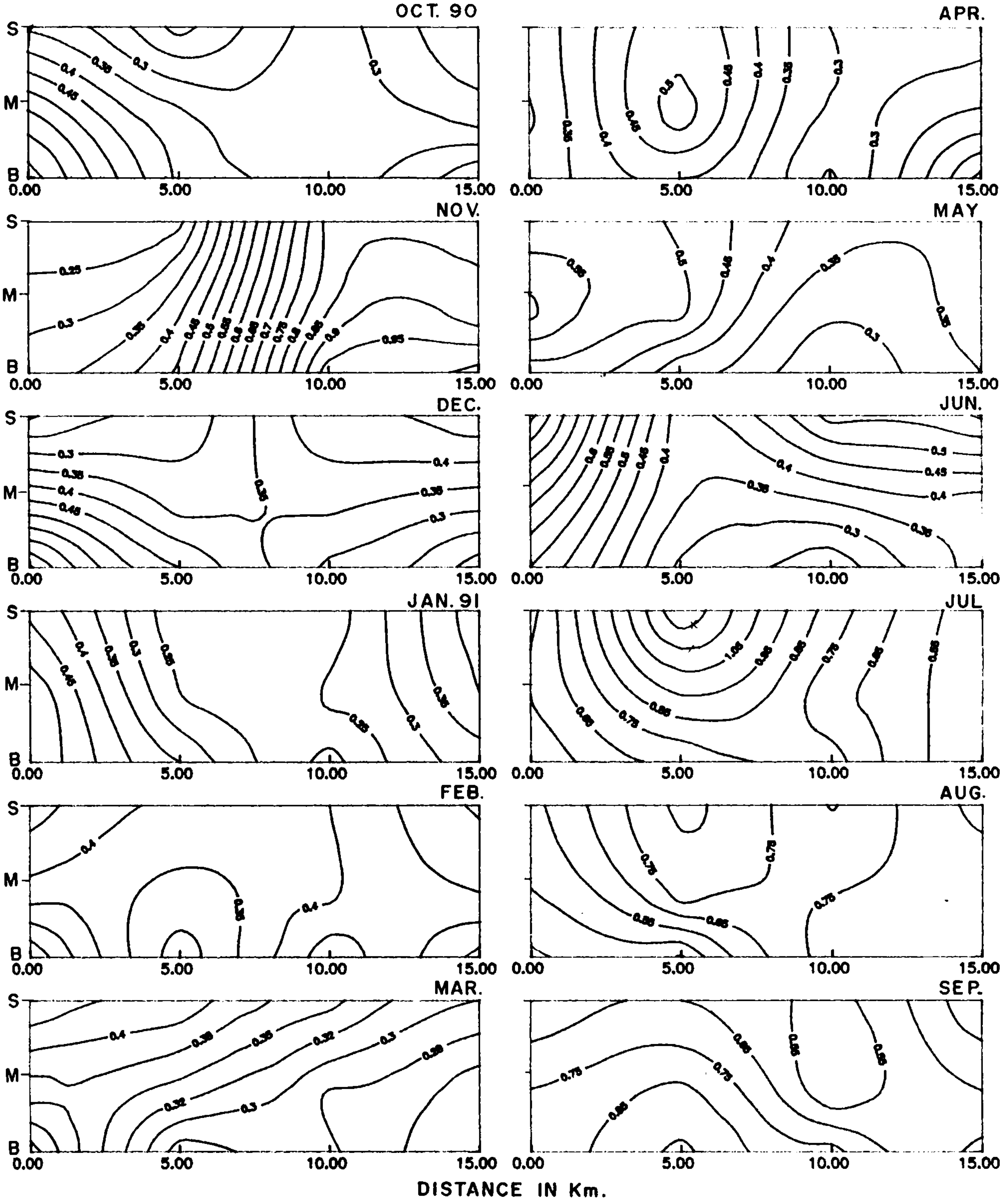


Fig. 4.2.5. Vertical profiles showing the distribution of organic phosphorus.

4.2.2.2. Organic Phosphorus

Seasonal variations in the integrated mean concentration organic phosphorus in the water column at different sections of the estuary are shown in Fig 4.2.4. Monthly vertical profiles of organic phosphorus distribution are shown in Fig 4.2.5.

The general trend observed in the seasonal and spatial distribution of organic phosphorus was inverse to that inorganic phosphate. Except during November, organic-P was uniformly distributed throughout the estuary in the post and pre monsoon periods. Comparatively higher concentrations and greater spatial variations were observed during the monsoon months. The maximum concentration of organic-P observed was 0.98 µgat/l at sections 3 and 4 during November. Except this and during certain monsoon months, organic-P decreased from the river mouth towards upstream and higher values were observed at the surface. Concentration of organic P was found to be very low (<0.5 µgat/l) throughout the estuary during the pre monsoon months.

4.2.3. Tidal variations in phosphorus distribution

Distribution of phosphorus in the estuary was found to vary within a tidal cycle and the tidal influence varied with seasons. During monsoon, the tidal influence was limited to section 1 only and inorganic phosphate was found increasing during the flood period and thereafter decreasing (Fig 3.2.6). An increase in concentration from surface to bottom

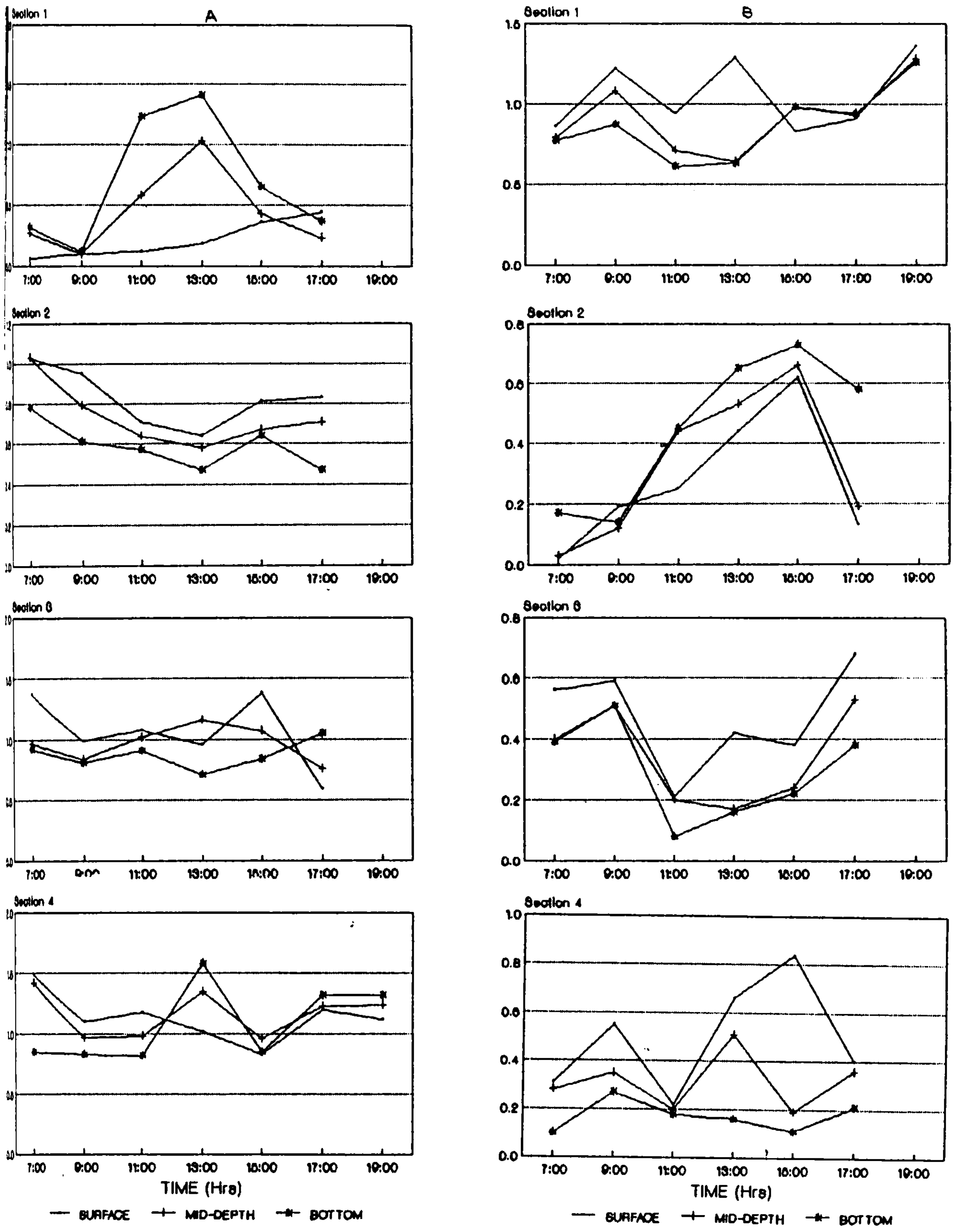


Fig.4.2.6. Tidal variations in inorganic phosphate (A) and organic-P (B) during post monsoon.

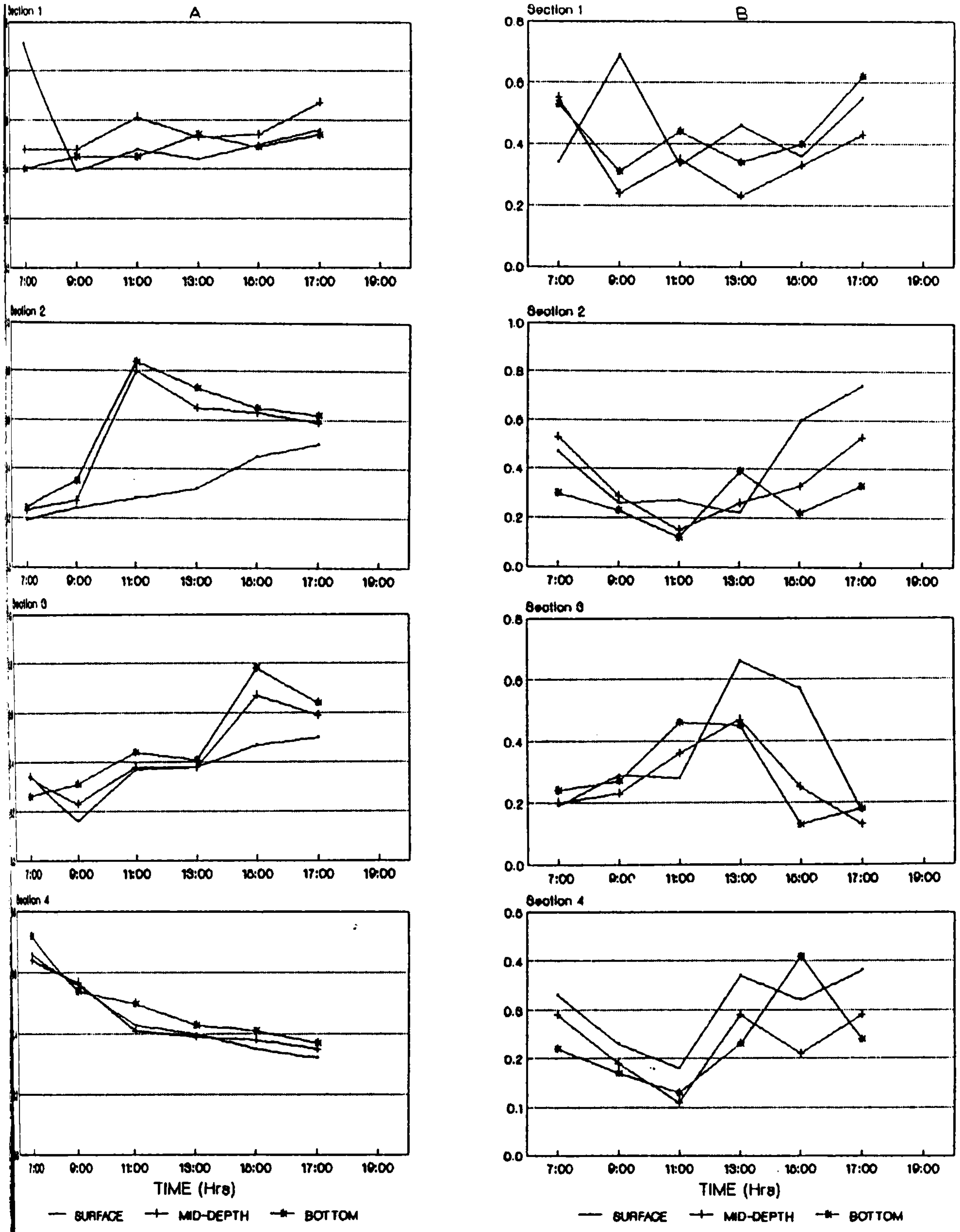


Fig.4.2.7. Tidal variations in inorganic phosphate (A) and organic-P (B) during pre monsoon.

was observed throughout the tidal cycle.

Inorganic phosphate concentration followed the tidal rythm at section 1 during the post monsoon season with a peak value towards the bottom at high tide (Fig 4.2.6). The reverse was the case at section 2 and no significant variation was observed at sections 3 and 4. The tidal variations observed for organic P was opposite to that of inorganic phosphate at sections 1 and 2. At section 1, organic-P was higher at the surface during flood tide and at section 2, it was higher at the bottom during the same period. At sections 3 and 4, higher concentrations of organic P were observed at the surface throughout the tidal cycle and the maximum values were during the ebb period.

During the premonsoon period, tidal variations of inorganic phosphate and organic P (Fig 4.2.7) were very small at section 1. At section 2, the peak value observed for inorganic phosphate was at the begining of the flood tide and it coincided with a minimum value for organic-P. The peak value of inorganic phosphate and the minimum concentration of organic-P at section 3 was after the flood period. At section 4, inorganic phosphate decreased with flood tide and organic phosphorus increased during the same period.

4.2.4. DISCUSSION

The temporal and spatial variation of inorganic phosphate differed from that of nitrogen fractions. The concentration that was generally low during the pre monsoon period picked up with the advent of monsoon and recorded the highest mean concentration during the post monsoon at all sections in the estuary. Except during December, January and June, higher concentrations of inorganic phosphate was found at the rivermouth section. Organic phosphorus was higher at the rivermouth except during November.

Therefore the source of inorganic phosphate as well as organic-P was mainly from the sea. Regeneration from sediments was found to be a major source during post monsoon season. The monsoon floods contributed only small amounts of phosphate to the estuary, which was apparent from the slight increase of phosphate concentration during June. The concentration was very low at sections 1 and 2 during this period and it can be correlated with the high values of interstitial phosphate. Jitts (1959) showed that 80 to 90% of the phosphate in solution might be adsorbed to the estuarine silt and this process is more under conditions of high terrestrial runoff. Higher interstitial phosphate concentrations at sections 1 and 2 during monsoon (Table 4.4.3) reveal this. High values of inorganic phosphate observed at the rivermouth during July and August could be due to the intrusion of upwelled water (see Chapter 3).

The high concentrations observed during December and January can be accounted as due to local regeneration under favourable physico-chemical conditions. Pomeroy et al. (1965) pointed out that the exchange of phosphate consisted of a two step ion exchange process between clay minerals and water, plus an exchange between terrestrial micro-organisms and water. Further he suggested that the exchange rate and capacity of the sediments were ecologically important factors in maintaining the phosphate concentration at an optimum level favourable for plankton production.

It has been found that total productivity in aquatic biological communities is directly limited by the concentration of available phosphorus and that several geochemical processes are involved in regulating the availability of phosphorus in the nutrient cycle. One of these important processes in the aquatic environment is the incorporation of phosphorus into the sedimental phase, either by sorption mechanisms or by the formation of insoluble inorganic phosphate minerals (Strom and Biggs, 1982). The biological removal of phosphate in estuaries include uptake by both phytoplankton and bacteria (Lebo, 1990). The 'buffering' of phosphate concentrations in estuaries has been described as an equilibrium process where phosphorus is adsorbed or released from particles to maintain a constant concentration.

The seasonal pattern of Chlorophyll'a' distribution (Fig.4.2.8) was generally the opposite of those of nitrate and phosphate, suggesting that the seasonal depletion of these inorganic nutrients, especially during the premonsoon months could be due to assimilation by phytoplankton.

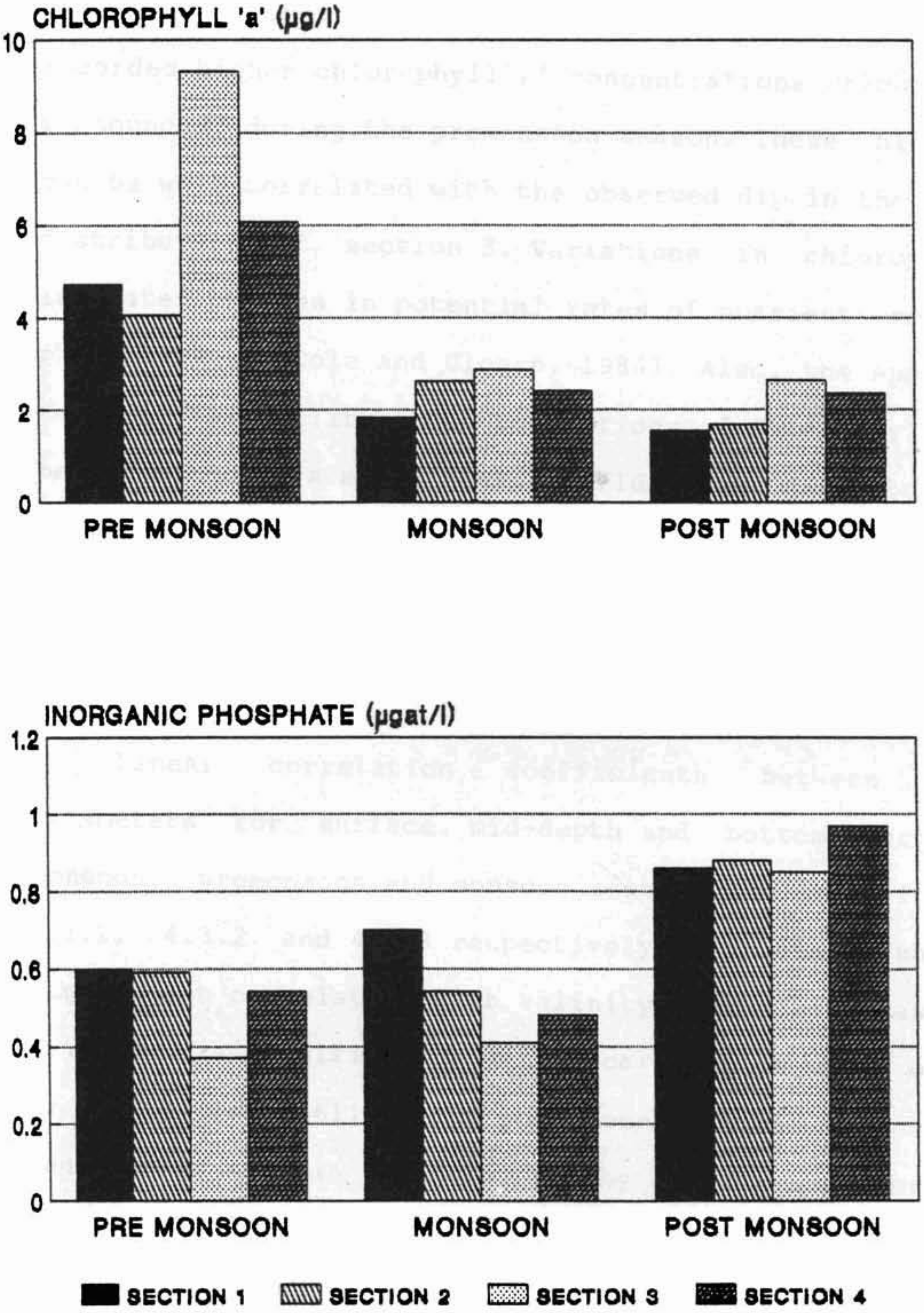


Fig.4.2.8. Seasonal averages of chlorophyll 'a' and inorganic phosphate at various sections in the estuary.

Compared to other sections studied in the estuary, section 3 recorded higher chlorophyll'a' concentrations which was more pronounced during the premonsoon season. These high values can be well correlated with the observed dip in the phosphate distribution at section 3. Variations in chlorophyll 'a' indicate changes in potential rates of nutrient removal by phytoplankton (Cole and Cloern, 1984). Also, the spatial and temporal variability in concentrations of Chlorophyll'a' can be examined as a major factor influencing distributions of nutrients supplied by river and other sources (Schemel and Hager, 1986).

4.3. Inter-relationship between various parameters.

Linear correlation coefficients between various parameters for surface, mid-depth and bottom during post monsoon, premonsoon and monsoon seasons are given in tables 4.3.1, 4.3.2 and 4.3.3 respectively. Ammonia-N showed no significant correlation with salinity during all seasons, but it showed a significant negative correlation with organic-N ($r = -0.54$ to -0.61) during post monsoon. This indicated the addition of ammonia to the system by other means. Perhaps due to ammonification in the water column in which ammonia is produced by the bacterial decomposition of nitrogenous organic compounds.

Significant negative correlation ($r = -0.50$ to -0.86) was obtained for nitrate-N with salinity during all seasons, showing the source of nitrate to be land-derived. Nitrate-N

Table 4.3.1. Linear Correlation Coefficients - Post monsoon

SURFACE

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.35	-0.61**	0.36	-0.09	-0.09
Nitrate		1	-0.76**	0.33	0.36	-0.51*
Organic N			1	-0.33	-0.22	0.19
Phosphate				1	-0.25	-0.14
Organic P					1	-0.58**
Salinity						1

MID-DEPTH

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	-0.04	-0.54**	-0.02	0.45*	0.25
Nitrate		1	-0.58**	0.63**	-0.19	-0.74**
Organic N			1	-0.26	-0.24	0.25
Phosphate				1	-0.39	-0.57**
Organic P					1	0.28
Salinity						1

BOTTOM

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.28	-0.59**	0.07	0.31	-0.08
Nitrate		1	-0.60**	0.54**	-0.21	-0.56**
Organic N			1	-0.18	-0.10	0.13
Phosphate				1	-0.44*	-0.70**
Organic P					1	0.49
Salinity						1

** Calculated r is significant at 1% level
* Calculated r is significant at 5% level

Table 4.3.2. Linear Correlation Coefficients - Premonsoon

SURFACE

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.16	0.15	0.48*	-0.18	-0.19
Nitrate		1	0.30	-0.14	-0.39	-0.55**
Organic N			1	-0.09	-0.21	-0.69**
Phosphate				1	-0.18	0.24
Organic P					1	0.52**
Salinity						1

MID-DEPTH

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.57**	0.42	0.13	0.19	-0.26
Nitrate		1	0.60**	0.19	-0.23	-0.55**
Organic N			1	-0.12	-0.35	-0.86**
Phosphate				1	-0.21	0.33
Organic P					1	0.47*
Salinity						1

BOTTOM

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.56**	-0.02	0.10	0.24	-0.08
Nitrate		1	0.28	0.09	-0.14	-0.50*
Organic N			1	-0.03	-0.32	-0.67**
Phosphate				1	-0.26	-0.17
Organic P					1	0.56**
Salinity						1

** Calculated correlation coefficient (r) is significant at 1% level
* Calculated correlation coefficient (r) is significant at 5% level

Table 4.3.3. Linear Correlation Coefficients - Monsoon

SURFACE

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.43*	-0.19	-0.14	0.23	0.05
Nitrate		1	-0.15	-0.35	0.33	0.03
Organic N			1	0.18	0.07	0.10
Phosphate				1	-0.26	0.52**
Organic P					1	0.52
Salinity						1

MID-DEPTH

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.16	-0.11	0.13	-0.16	0.12
Nitrate		1	0.59**	0.01	0.14	-0.69**
Organic N			1	0.34	-0.15	0.61**
Phosphate				1	-0.28	0.14
Organic P					1	-0.14
Salinity						1

BOTTOM

	Ammonia	Nitrate	Organic N	Phosphate	Organic P	Salinity
Ammonia	1	0.19	-0.21	-0.23	-0.07	-0.10
Nitrate		1	-0.39	0.09	0.25	-0.86**
Organic N			1	0.60	-0.12	0.40
Phosphate				1	-0.32	0.02
Organic P					1	-0.14
Salinity						1

** Calculated correlation coefficient (r) is significant at 1% level
* Calculated correlation coefficient (r) is significant at 5% level

showed a clear inverse relationship with organic-N during post monsoon whereas the relation was irregular during pre monsoon and monsoon seasons.

Organic-N was positively correlated with salinity during monsoon and post monsoon ($r = 0.40$ to 0.61). This indicated that the source of this nutrient during this period was from the sea. Dissolved organic compounds in the sea water come from the decay of organic matter produced in the body of water itself, from the excreted waste products of living organisms or by diffusion from the bodies of certain phytoplankton (Rao and Rao, 1974).

Significant inverse correlation ($r = -0.67$ to -0.86) was obtained for organic-N with salinity during pre monsoon. Salinity was high throughout the estuary with values varying between 30 and 35 X 10^{-3} in the lower part (0 - 5 Km region) of the estuary and between 20 and 25 X 10^{-3} in the upstream (10 - 15 Km) region. Organic-N showed an increasing trend from the lower to the upper region of the estuary and it was maximum at section 4 during the pre monsoon months. Since high organic-N indicate higher productivity, the upper estuary could be more productive during this period. Chlorophyll 'a' values were also high during this period (K. Saraladevi, personal communication). Laboratory experiments on many organisms collected from the inshore waters of the south-west coast of India have shown that optimum photosynthesis occurs at salinities ranging from 10 to 20 X 10^{-3} (Qasim et al., 1972).

It is well known that organic-N in dissolved form may be available for the direct utilisation by phytoplankton to some extent. Verlencar (1984) has reported that the large portion of organic-N available in the estuarine and coastal waters of Goa serve directly or indirectly as the efficient nutrient supplement for the primary producers. Many marine invertibrates possess the ability to take up dissolved organic compounds from sea water. In fresh water invertibrates uptake proceeds at a considerably lower rate or is completely absent (Sepers, 1977). Thus, the decrease in concentration of organic-N in the lower reaches of the estuary could be also due to higher biological uptake.

Inorganic phosphate showed significant negative correlation with salinity during post monsoon, especially at the bottom ($r = -0.70$) and the relationship was irregular during other seasons. Since the high concentration of inorganic phosphate during post monsoon was attributed to transfer from the interstitial water, its negative correlation with salinity indicates that the process is favoured by decrease in salinity. High phosphate concentration in the upstream section during this period reveals this. Correlation of phosphate with organic-P was always negative and the values were low ($r < -0.44$). Significant positive correlation was found between organic-P and salinity ($r>0.50$) except in the bottom during monsoon and in the surface during post monsoon.

Results of analysis of variance for 3-way classification

Table 4.3.4. Analysis of variance for 3-way classification using 3 factors.

	SALINITY			AMMONIA-N			ORGANIC-N		
Source	F value	d.f.	Remarks	F value	d.f.	Remarks	F value	d.f	Remarks
Between seasons	69.90	2	**	9.89	2	**	17.57	2	**
Between depths	28.37	2	**	3.34	2	*	8.92	2	**
Between time and locations	35.60	23	**	7.93	23	**	3.98	23	**
Interaction effect of:-									
(1) Seasons X depths	9.51	4	**	2.05	4	NS	1.12	4	NS
(2) Depths X time	0.95	46	NS	0.77	46	NS	1.10	46	NS
(3) Seasons X time	0.93	46	NS	5.05	46	**	9.39	46	**
Error		92			92			92	
Total		215			215			215	

** Calculated F is significant at 1 % level (P > 0.01)

* Calculated F is significant at 5 % level (P > 0.05)

NS Not significant.

Table 4.3.5. Analysis of variance for 3-way classification using 3 factors.

	NITRATE-N			PHOSPHATE			ORGANIC-P		
Source	F value	d.f.	Remarks	F value	d.f.	Remarks	F value	d.f	Remarks
Between seasons	74.16	2	**	9.35	2	**	3.43	2	*
Between depths	17.41	2	**	0.74	2	NS	3.96	2	*
Between time and locations	4.99	23	**	6.17	23	**	1.93	23	*
Interaction effect of:-									
(1) Seasons X depths	5.42	4	**	3.63	4	**	2.45	4	NS
(2) Depths X time	0.97	46	NS	1.01	46	NS	0.92	46	NS
(3) Seasons X time	4.60	46	**	7.46	46	**	2.37	46	**
Error		92			92			92	
Total		215			215			215	

** Calculated F is significant at 1 % level ($P > 0.01$)

* Calculated F is significant at 5 % level ($P > 0.05$)

NS Not significant.

using three factors, viz. seasons, depths and stations, are given in tables 4.3.4 and 4.3.5. In the case of all parameters significant difference was found between seasons and and between stations, but the variation in the concentration of all parameters were independent of depth. The interaction between seasons and depths, and depths and stations were insignificant in all cases except that of nitrate and phosphate, where the interaction between seasons and depths was found to be high.

N:P ratio varied spatially and seasonally reflecting the contrasting patterns of nitrate and phosphate variations. At section 1, the ratio varied from 2.3 (in April) to 97.6 (in June). At section 2, the variation in the N:P ratio was from 0.69 in March to 90.9 in August. At sections 3 and 4, the ratio was lowest in February (3.6 and 1.8 respectively) and and highest (125 and 132.5 respectively) in August. The large shifts in N:P ratios have significant implications to the fate of these nutrients in the estuary. The influence of river discharge bringing in large amounts of nitrate during the south-west monsoon period (June - September) is well reflected at all sections with high N:P ratios.

The consumption of nitrate and the production of phosphate greately reduces the ratio in the lower estuary during the post and pre monsoon seasons. The much lower N:P ratios encountered at section 2 during premonsoon can be explained as due to loss of nitrogen through denitrification.

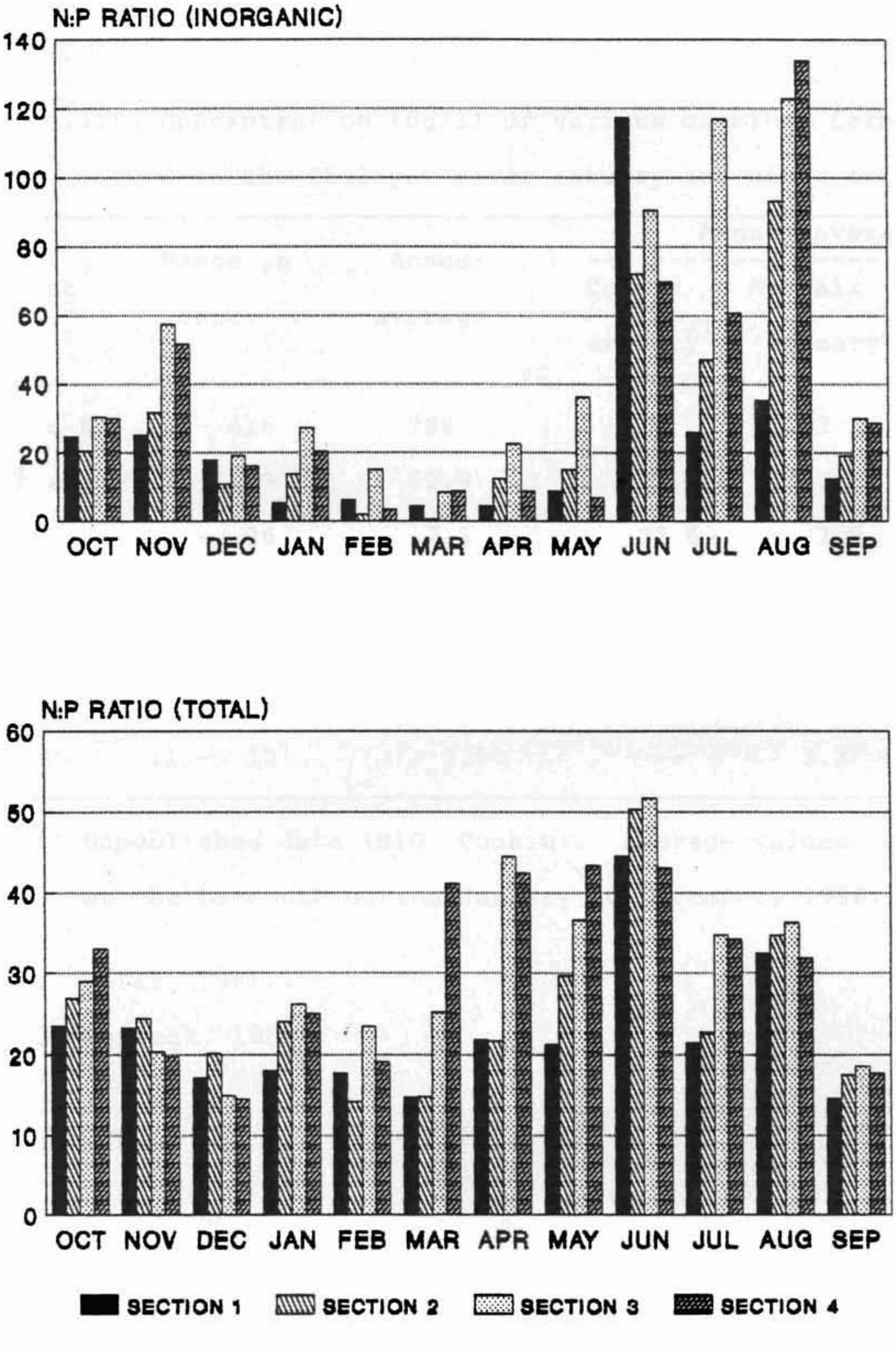


Fig.4.3.1. N/P ratio of inorganic and total nutrients at various sections in the estuary.

Table 4.3.6. Concentration (μg/l) of various chemical forms of N and P in the Chaliyar river estuary and other estuaries.

Nutrient	Range in conc.	Annual average	Annual average		
			Cochin estuary[1]	Morlaix estuary[2]	Unpolluted Rivers[3]
Nitrate-N	15 - 616	200	277	252	100
Ammonia-N	0 - 259	52.9	123.2	62	15
Nitrite-N	0 - 26	7.5	27.6	7.8	1.5
Organic-N	25 - 350	150	375	102	260
Phosphate	7 - 53	20.2	94.8	61	12.5
Organic-P	7 - 31	15.2	92.6	22	15
Chl 'a'	.1 - 12	3.9	--	3.3	--

1 Unpublished data (NIO, Cochin). Average values observed at the barmouth during January to December, 1990.

2 Wafar, 1981.

3 Meybeck, 1982.

The N:P ratio of total nutrients showed much less variation throughout the year compared to that of inorganic nutrients (Fig 4.3.1). TN:TP ratio at all sections varied between 14 and 50 during the period of investigation. The relatively constant value of TN:TP ratio around 20 reflected the complex overall chemical-biological balance in the system and it was only during times of intense rainfall and river discharge, the ratios varied greatly from this figure.

A comparison of annual averages of nutrients in the Chaliyar river estuary with that of other estuaries and unpolluted rivers are given in Table 4.3.6.

4.4. The sediment-water exchange of nutrients

The exchange of dissolved substances across the sediment-water interface is an important process affecting the chemical composition of estuaries (Pomeroy et al., 1965; Hale, 1975). Sediment-water fluxes are described as important nutrient sources (Boynton et al.,1980; Callender and Hammond, 1982; Fisher et al., 1982; Boynton and Kemp, 1985) and sediment fluxes may also constitute a major sink for nutrients in the water column (Boynton et al., 1980; Callender and Hammond, 1982). Riverine sediment loading may also affect sediment-water nutrient fluxes by addition of organic matter or particle adsorbed inorganic nutrients or by effects on redox equilibria (Teague et al., 1988).

Mineralization of organic matter in bottom deposits of natural waters causes the interstitial water to be enriched in various nutrients as compared to the overlying water. By means of molecular diffusion and other mixing processes there is a continuous transport of nutrients between the sediment and overlying water (Rutgers, 1980). Therfore, the bottom is not only a sink for organic particles but also a source of their soluble decomposition products like nutrients. The very high nutrient regeneration rates of many nearshore sediments result from relatively large local primary productivity and relatively short residence times of planktonic detritus in the water column prior to deposition (Ullman and Sandstrom, 1987).

In shallow systems the important part of nutrient cycling occurs in the benthic phase rather than in the water column. This has been explained as due to high standing stock of organic matter and the fluctuation in the rate of benthic recycling (Billen, 1978). Therefore the measurements of nutrients in the interstitial water becomes important. The dissolved nutrients in the interstitial water reflect the combined effects of the biological and chemical processes producing or consuming nutrients and the various physical forces affecting the transfer of the dissolved species. In shallow coastal waters the sediment nutrient exchange strongly influences the water column nutrient chemistry (Nixon, 1981).

The sediment characteristics at various sections of the estuary are given in Table 4.4.1. The seasonal distribution of various fractions of nitrogen and phosphorus in the

Table 4.4.1. Sediment characteristics of various sections in the Chaliyar River Estuary.

Sections	Texture (%)			Eh (mV)
	Sand	Silt	Clay	
PRE MONSOON				
S-1	64.80	22.30	12.90	-140
S-2	66.30	20.60	13.20	-156
S-3	92.50	6.00	1.50	110
S-4	90.40	7.45	2.15	95
MONSOON				
S-1	71.45	26.20	2.35	-165
S-2	70.10	28.40	1.50	-145
S-3	99.70	0.30	0.00	105
S-4	99.50	0.50	0.00	115
POST MONSOON				
S-1	72.25	17.55	10.20	110
S-2	78.95	16.25	4.80	105
S-3	95.60	3.85	0.55	185
S-4	94.45	4.75	0.80	180

Table 4.4.2. Nitrogen and Phosphorus contents of sediment samples from various sections in the Chaliyar River Estuary.

Sections	Concentration (µg/g)		N:P Ratio
	Total N	Total P	
PRE MONSOON			
S-1	1798.2	1215.0	1.48
S-2	2387.4	1497.0	1.59
S-3	2.2	206.4	0.01
S-4	6.5	153.7	0.04
MONSOON			
S-1	3075.0	1329.5	2.31
S-2	2823.3	1556.3	1.81
S-3	24.2	111.5	0.21
S-4	66.6	98.1	0.67
POST MONSOON			
S-1	2386.8	1762.2	1.35
S-2	1160.4	936.5	1.24
S-3	3.3	193.1	0.02
S-4	8.5	131.0	0.06

Table 4.4.3. Interstitial nutrients of sediments at various sections in the Chaliyar River Estuary

Sections	Nutrient Concentrations (µgat/l)			
	Nitrite-N	Nitrate-N	Ammonia-N	Phosphate
PRE MONSOON				
S-1	1.70	13.09	559.90	14.44
S-2	1.92	12.35	681.70	12.43
S-3	3.59	73.90	106.20	2.46
S-4	1.93	17.35	69.30	8.28
MONSOON				
S-1	1.75	16.41	770.00	22.20
S-2	3.29	29.72	480.00	23.70
S-3	1.64	42.28	118.40	1.20
S-4	1.48	36.85	86.20	1.64
POST MONSOON				
S-1	2.37	15.52	425.90	11.08
S-2	1.45	13.16	226.60	9.51
S-3	1.33	61.62	51.52	3.25
S-4	1.88	24.92	27.80	4.92

sediment and interstitial water are given in Tables 4.4.2 and 4.4.3.

The nitrogen and phosphorus content of sediments as well as interstitial water samples showed much higher concentrations in the lower part (sections 1 and 2) of the estuary compared to the upper region (sections 3 and 4). This observation can be directly linked with the sediment characteristics of the estuary. Sediments of sections 1 and 2 contain more clay and silt percentage and so are capable of retaining and recycling nutrients compared to sections 3 and 4 which are composed of 90-99% sand. Thus the lower part of the estuary is a more active zone with respect to biogeochemical processes.

On a perusal of the results of various nitrogen fractions in the interstitial water indicated that ammonia formed the major component than nitrate or nitrite. The high amount of ammonia observed in the lower part of the estuary was due to active regeneration from sediment. The distribution of nitrate in the interstitial water showed much lower values at sections 1 and 2 irrespective of the season. The decrease in concentration could be explained as due to nitrate reduction to ammonium and incorporation into the sediment. Higher ammonia-N concentrations and lower redox potentials (Table 4.4.1) observed in these sections favoured this argument. Nitrate reduction to ammonium and organic nitrogen in estuarine sediments increased markedly with decrease in redox potential (Buresh and Patrick, 1981).

Higher nitrate concentrations observed in the upper region of the estuary may also be due to nitrification by nitrifying organisms of terrigenous origin (Verstraete and Alexander, 1973; Billen, 1975). Billen (1975) observed that these nitrifying bacteria grew more slowly in saline media and the nitrifying population in the estuary is mostly made up of freshwater bacteria. Although the data on the bacterial population of the estuary is available, in the absence of data on nitrosomonas distribution no definite conclusion can be drawn on the nature of nitrification process. The high values of interstitial ammonium observed during monsoon could also be due in part to suppression of nitrification at low temperatures as reported by Berounsky and Nixon (1990).

Phosphate concentration in the interstitial water was found to be maximum during monsoon. Perhaps it is the result of tide effect. The maximum concentration corresponding to the rememberance of the composition of the overlying water at high tide which has a higher phosphate content than at low water. Adsorption of phosphate to the silty sediment also helps in the accumulation. Decrease in phosphate concentration in the interstitial water during post monsoon was due to its release to the overlying water. In the sediment as well as in the interstitial water, phosphate concentration was minimum at section 3 throughout the year and this can be correlated with the very low silt percentage of the sediment at this section.

CHAPTER 5

NUTRIENT FLUX STUDIES

5. NUTRIENT FLUX STUDIES

An important feature of the estuarine flow systems is the great spatial and temporal variation resulting from interaction between tidal oscillation and fresh water inflow. Nutrients and suspended sediments are transported to estuaries through rivers. Measurement of the fluxes of biologically important elements such as carbon, nitrogen and phosphorus have begun with the realization that the biological productivity of estuaries and nearshore waters are determined by the river addition of nutrients. Nutrient fluxes depend on the vertical distribution of velocities and concentrations, and the location of the source. Cross-sectional variations in velocity and nutrient concentrations have a significant effect on the longitudinal fluxes.

Several studies have been focussed on nutrient fluxes in estuaries, and of those, majority were in tidal or brackish marshes (eg., Valiela et al., 1978; Woodwell et al., 1979; Nixon, 1980; Daly and Mathieson, 1981; Jordan et al., 1983; Wolaver et al., 1983; Witing et al., 1985; Spurrier and Kjerfve, 1988; Correll et al., 1992). The transport of nutrients and carbon from the Nanaimo River to its estuary and a comparison of carbon input to insitu primary production were presented by Naiman and Sibert (1978). Lesack et al. (1984) have reported the fluvial transport of carbon, nitrogen and phosphorus by the Gambia river as a function of discharge. Wilmot et al. (1985) have calculated the nutrient transport rates through Himmerfjard (a Swedish estuary) and presented the nutrient budget for 78 days autumn measurement period. Results of investigations to measure the direction and magnitude of fluxes of dissolved nutrients between an intertidal mudflat and suspended sediment and the water column within Cumberland basin are reported by Keizer et al. (1989).

The concentration and transport of carbon, nitrogen and phosphorus in the Morlaix river and their relationship with primary productivity of the estuarine waters was discussed by Wafar et al. (1989). Stern et al. (1986; 1991) have measured seasonal nutrient and suspended solid fluxes in a riverine influenced, tidal freshwater bay in Louisiana. Their study showed that seasonal variation in flux of each material was resulted from changes in both water flux and seasonal nutrient concentration. Park and James (1990) have reported a method for estimating the flux of solutes in a cross-section based on the hourly countours of salinity and velocity and for explaining the mass transport mechanism in estuaries. Jordan et al. (1991) have estimated the fluxes of nutrients between the upper and lower parts of the Rhode River estuary using a mixing model with chloride as a conservative tracer.

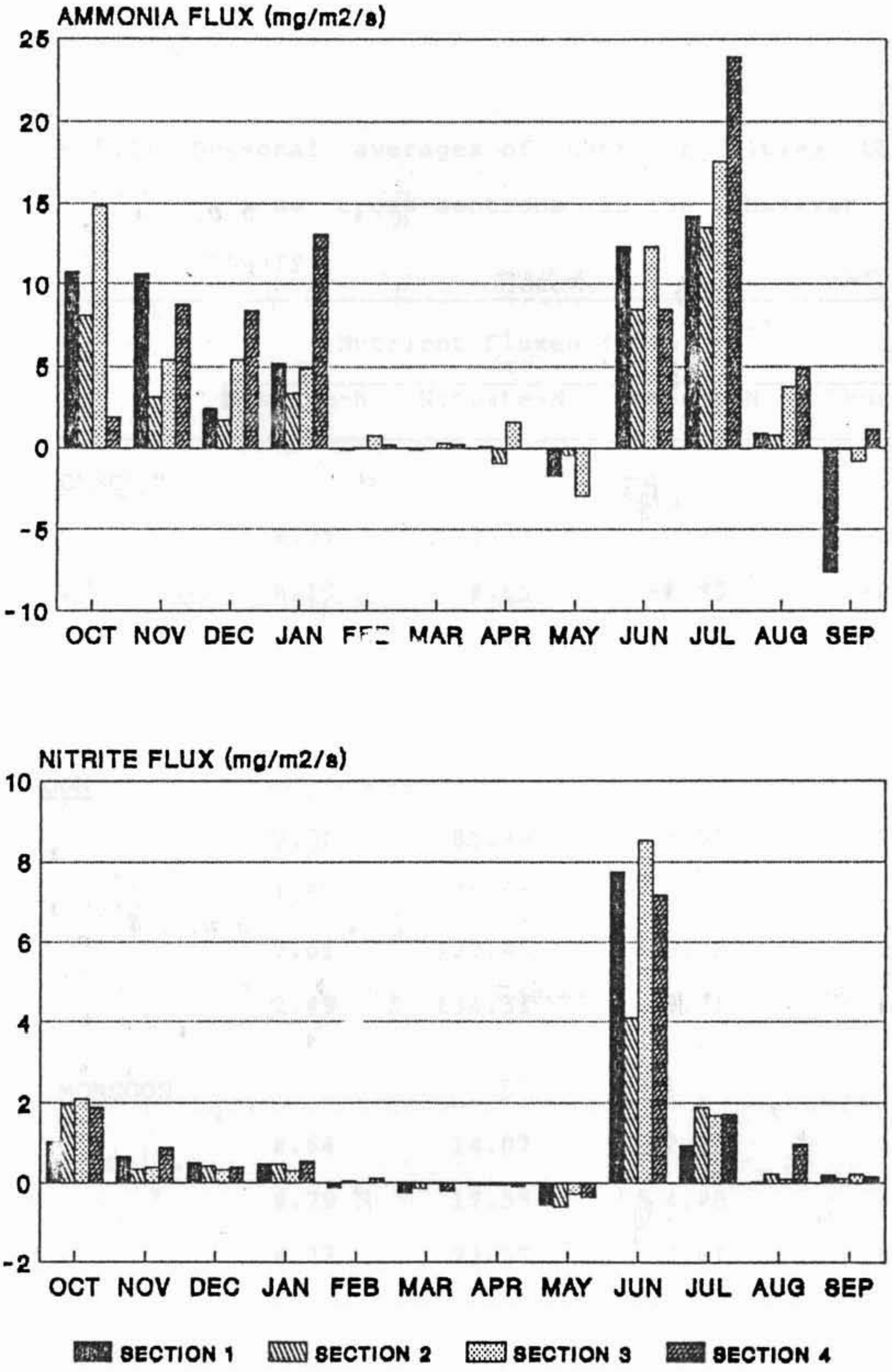
Nutrient flux studies from Indian estuaries have not been reported so far. Therefore an attempt has been made here to study the nutrient fluxes through four cross-sections in the Chaliyar River estuary. Net fluxes of nitrite-N, nitrate-N, ammonia-N and inorganic phosphate were estimated and the results were analysed to determine the relative influences of riverine and tidal forcing on the fluxes.

Net fluxes of inorganic nutrients through the four cross-sections in the estuary are schematically represented in Figs. 5.1 and 5.2 and their seasonl averages are given Table 5.1. Net fluxes are represented as mg per m^2 of cross-sectional area. Use of this unit allows direct comparison of fluxes between various cross sections.

5.1. Ammonia Fluxes

Large net fluxes of ammonia-N were observed during the monsoon and postmonsoon seasons and very small positive or negative net fluxes were found during the premonsoon season. During the month of September, an exceptionally high negative flux (-7.60 mg $m^{-2}s^{-1}$) obtained at section 1. This can be explained as a result of the tidal input from the coastal waters. High amount of organic matter produced in the coastal areas due to bloom conditions as a result of upwelling (Venugopal et al., 1979) is transported to the estuary with the tide, the decay and decomposition of which results in high concentration of ammonia.

Average value of net fluxes during monsoon increased from 4.97 mg $m^{-2}s^{-1}$ at section 1 to 9.61 at section 4 and the quantity varied from 7.22 to 8.01 during the postmonsoon season. An increased input from the coastal waters can be observed as an increase in the flux rate at section 1



ig.5.1. Net fluxes (mg per m^2 of cross-sectional area per s) of ammonia and nitrite through various sections in the Chaliyar River Estuary.

Table 5.1. Seasonal averages of nutrient fluxes through various cross-sections in the Chaliyar River Estuary.

Sections	Nutrient Fluxes (mg m^{-2} S^{-1})			
	Nitrite-N	Nitrate-N	Ammonia-N	Phosphate
PRE MONSOON				
S-1	-0.24	-2.92	-0.47	-0.09
S-2	-0.19	-0.65	-0.35	-0.26
S-3	-0.08	-0.97	-0.08	-0.12
S-4	-0.13	-0.16	0.10	-0.26
MONSOON				
S-1	2.21	81.09	4.97	3.52
S-2	1.57	79.60	5.67	3.14
S-3	2.61	122.46	8.20	2.92
S-4	2.49	134.31	9.61	4.63
POST MONSOON				
S-1	0.64	14.87	7.22	1.87
S-2	0.79	17.55	4.08	1.94
S-3	0.77	23.57	7.61	2.42
S-4	0.91	33.23	8.01	2.82

compared to section 2. During the premonsoon period, ammonia-N was transported towards the river by tidal action and average values of net fluxes varied from -0.47 mg $m^{-2}s^{-1}$ at section 1 to 0.08 mg $m^{-2}s^{-1}$ at Section 3. At section 4, the net flux was directed downwards with an average value of 0.10 mg $m^{-2}s^{-1}$.

5.2. Nitrite fluxes

Net fluxes of nitrite-N were very small except during June and the maximum value was 8.50 mg $m^{-2}s^{-1}$ which was found decreasing after the peak monsoon period and the net fluxes were directed towards upstream during the premonsoon season. Seasonal averages showed generally higher positive values in the upstream sections which indicated the source of this nutrient to be land derived and its magnitude was found very low and varying due to its unstable oxidation state.

5.3. Nitrate fluxes

The seasonal variation in the magnitude of net fluxes were exactly similar to that of variation in concentration of nitrate-N. A gradual decrease in the net fluxes from the riverine end towards the marine end of the estuary was observed and the direction of the net fluxes were always towards the sea during the monsoon and post monsoon seasons. This clearly indicated the riverine source of nitrate-N as evidenced from other observations. An average net flux as high as 134.31 mg $m^{-2}s^{-1}$ was found at section 4 whereas it was 81.09 mg $m^{-2}s^{-1}$ at section 1 during monsoon. During the

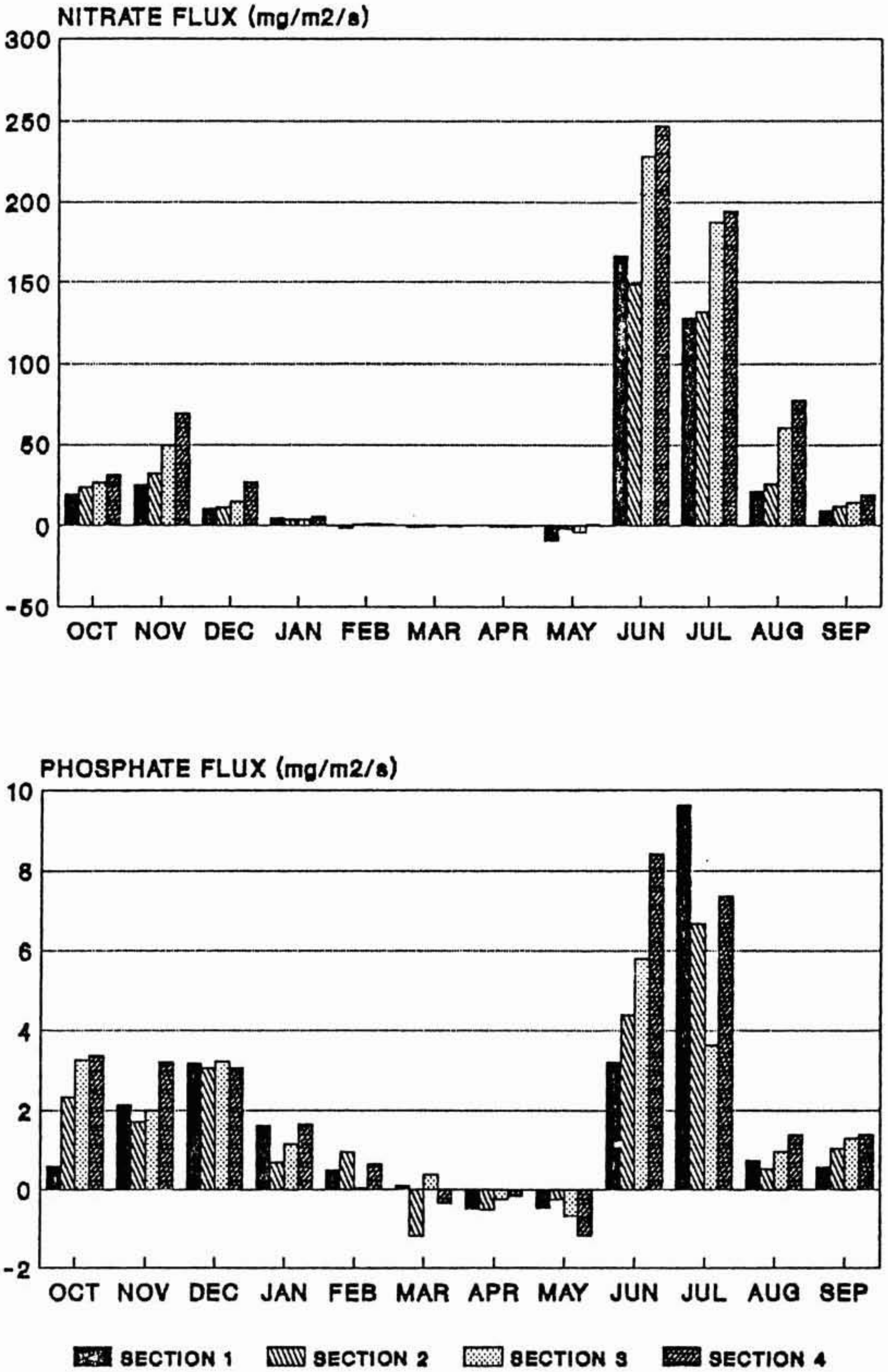


Fig.5.2. Net fluxes (mg per m^2 of cross-sectional area per s) of nitrate and phosphate through various sections in the Chaliyar River Estuary.

post monsoon season it was 33.23 and 14.87 mg $m^{-2}s^{-1}$ respectively. The reverse was the trend during premonsoon. The net fluxes were directed towards the river and their magnitude decreased towards upstream. A change in the direction of net fluxes were also observed in the upstream sections showing small positive values. Average net fluxes varied from -2.92 mg $m^{-2}s^{-1}$ at section 1 to -0.16 mg $m^{-2}s^{-1}$ at section 4.

5.4. Phosphate Fluxes

The magnitude of net fluxes generally increased from the marine end towards the riverine end of the estuary with some exceptions. The most notable exception was during July when the net flux was maximum at section 1 and this was found due to the incursion of phosphate rich upwelled water to the estuary. Average of the net fluxes during monsoon varied from 3.52 at section 1 to 4.63 at section 4 and 1.87 at section 1 to 2.82 mg $m^{-2}s^{-1}$ at section 4 during the post monsoon period. The net fluxes were very small during the pre monsoon season and were directed towards the river. The decrease in the net fluxes may be explained by biological utilisation and also by other physico-chemical processes such as adsorption to particles, in suspension as well in sediment, regeneration etc.

5.5. DISCUSSION

Nutrient flux studies indicated that except during the premonsoon period there was a net transport of inorganic nutrients into the sea and the rate of this transport was mainly controlled by the river flow. The tidal action is opposing the riverine influence which is reflected in the magnitude and direction of net fluxes studied at four cross-sections in the estuary.

Due to the greater tidal influence and mixing and diffusion processes, net fluxes in the downstream sections are less than that of the upstream sections. Other possible mechanisms which reduce the net fluxes towards the marine end are biological uptake, adsorption to sediment and incorporation into the interstitial waters. Nutrient data from sediment samples and interstitial water also showed much higher values (Tables 4.4.2 and 4.4.3) at sections 1 and 2 as compared to sections 3 and 4. This also is related to the sediment characteristics of the estuary (Table 4.4.1). Sediments of sections 1 and 2 contain more clay and silt percentage favouring higher adsorption than at sections 3 and 4 where sand fraction form the major component of the sediment. Release of phosphate from the sediment to the overlying water also vary at different sites of the estuary depending on the bacterial activity and the physico-chemical conditions of the sediment. Similar variations were observed in Cochin backwater by Reddy and Sankaranarayanan (1972).

Table 5.2. Mean annual net flux of nutrients (mg per m^2 of cross-sectional area per s) at the river mouth (section 1) and upstream (section 4) of Chaliyar river estuary, Atchafalaya river and Willow Bayou.

Nutrient	Chaliyar River Estuary		Atchafalaya	Willow
	Section 1	Section 4	River*	Bayou*
Nitrate-N	31.01	55.79	470	80
Ammonia-N	3.90	5.90	10	10
Phosphate	1.76	2.39	20	5

* from Stern et al., 1991.

Table 5.2. shows that net flux per m^2 of cross-sectional area increases as riverine influence increases. In Chaliyar river estuary, tidal forcing is more at section 1 and the values are much closer to that of Willow Bayou than Atchafalaya river.

Transport of nitrate-N, ammonia-N and inorganic phosphate through various cross-sections in the estuary are presented as g s^{-1} in Table 5.3. Since the values were considerably low, nitrite-N was ignored. Transport of nutrients were directed towards sea during monsoon and postmonsoon months, and was directed towards the river during premonsoon. Considerable quantities of nutrients are transported through the estuary during October and November which was the period of north-east monsoon. The quantity decreased during December and was minimum during January.

Table 5.3. Nutrient transports (g s^{-1}) through various cross-sections in the Chaliyar river estuary.

	SECTION 1			SECTION 2			SECTION 3			SECTION 4		
	Nitrate-N	Ammonia-N	Phosphate	Nitrate-N	Ammonia-N	Phosphate	Nitrate-N	Ammonia-N	Phosphate	Nitrate-N	Ammonia-N	Phosphate
OCT	22.05	12.26	0.65	24.21	8.34	2.39	24.34	13.45	2.97	23.00	1.39	2.48
NOV	27.94	11.85	2.39	32.65	3.21	1.75	44.60	4.86	1.82	49.66	6.28	2.30
DEC	12.04	2.74	3.66	11.82	1.81	3.17	13.30	4.91	2.96	20.05	6.21	2.27
JAN	4.95	5.51	1.24	3.28	3.29	0.69	3.02	4.24	1.01	3.79	9.06	1.15
FEB	-1.66	-0.14	0.50	0.40	0.05	0.88	0.93	0.64	0.04	0.21	0.15	0.44
MAR	-1.23	-0.16	0.09	-0.41	0.00	-1.23	-0.25	0.26	0.35	-0.39	0.15	-0.26
APR	-0.21	0.09	-0.47	-0.35	-0.85	-0.45	-0.61	1.27	-0.21	-0.44	0.00	-0.11
MAY	-9.08	-1.76	-0.48	-2.12	0.45	-0.26	-3.34	-2.50	-0.56	0.19	0.00	-0.77
JUN	175.70	13.05	3.37	143.90	8.21	4.23	196.70	10.63	5.00	168.30	5.83	5.75
JUL	141.60	14.66	10.71	133.20	13.67	6.72	167.50	15.65	3.24	139.80	17.19	5.28
AUG	20.60	0.88	0.71	23.90	0.71	0.47	49.24	3.18	0.80	49.28	3.09	0.88
SEP	8.77	-7.35	0.53	10.46	-0.13	0.93	11.58	-0.66	1.06	11.75	0.72	0.87

Negative sign indicates transport towards the river.

Transport was directed towards the river during the premonsoon months (February to May) and maximum upstream transport was observed during May. Negative transport was comparatively higher at section 1 due to greater tidal forcing there. Maximum river transport of nutrients occurred during June-July, which was also the period of heavy rain fall and maximum river discharge. Transport decreased during August and September due to decrease in riverine forcing. The increased transport through section 1 compared to section 2 during the high runoff periods could be attributed to the influence of Chaliyam river which enters into the estuary near section 1 (see Fig. 2.1).

A comparison of nutrient transport rates through the upstream and downstream cross-sections of the estuary indicated some amount of utilization or retention by the estuarine system. This has resulted from a combination of various physical, chemical and biological processes taking place in the estuary. Eventhough there is some utilization of dissolved nutrients within the estuary, very large quantities of these are transported to the sea. For example, during the peak south-west monsoon period the amount of nitrate-N flushed out into the Arabian Sea through the Chaliyar river estuary after utilization is estimated to be 13.7 tons per day (average for June-July 1991) and the corresponding values for ammonia-N and inorganic phosphate are 1.2 and 0.61 tons per day respectively.

CHAPTER 6

SUMMARY

6. SUMMARY

A systematic and comprehensive study on the general hydrography and nutrient chemistry of Chaliyar river estuary was made together with an attempt to study the fluxes of inorganic nutrients through various cross-sections in the estuary. General hydrographic parameters include temperature, salinity, pH and dissolved oxygen. Various chemical forms of nitrogen and phosphorus studied include urea-N, ammonia-N, nitrite-N, nitrate-N, organic-N, inorganic phosphate and organic-P. Interstitial water samples were analysed to estimate ammonia-N, nitrite-N, nitrate-N and inorganic phosphate. Eh, sand-silt-clay percentage and total nitrogen and phosphorus content of sediment samples were also determined. Salient features of the investigation are summarised as follows.

The important factors affecting the general hydrography of estuaries in general and Chaliyar in particular are rainfall, freshwater inflow, and intrusion of seawater through the river mouth. Temperature was lowest during the monsoon months, increased gradually during postmonsoon and reached the maximum values during premonsoon. The annual variation in temperature was 8.2°C. Low temperature observed at the river mouth section during August was due to the intrusion of upwelled water. Temperature of the estuarine waters showed very little variation with tide except during monsoon.

Salinity was mainly controlled by freshwater discharge through the river. During the monsoon months when the river discharge was maximum, saline intrusion was felt upto a distance of about 5Km upstream from the river mouth. Seawater intrusion increased during post monsoon and the estuary was found to be marine dominated during premonsoon. The present observations on salinity distribution lead to the classification of the estuary to be a salt wedge type during monsoon, a partially mixed type during post monsoon and a well-mixed type during premonsoon. The variations in salinity during a tidal cycle was found to follow the tidal rythm.

The distribution of pH clearly indicated that the low pH values during the monsoon months are due to heavy fresh water inflow. The increased pH values as the season progressed are due to higher seawater intrusion and may also be due to the removal of carbon dioxide by photosynthetic activity which is higher during the pre and post monsoon months.

Dissolved oxygen concentration was higher during monsoon and comparatively lower during certain months of pre and post monsoon seasons. Low oxygen values observed at the bottom of section 1 during August indicated the presence of upwelled water. Lower oxygen values during the pre and post monsoon months could be attributed to the low freshwater inflow and also to higher utilisation by organic matter.

The contribution of various nitrogen fractions to the total-N pool of the estuarine waters were found to vary spatially and temporaly. Contribution of urea-N was minimum during premonsoon season at all sections. It was maximum in the upstream sections during monsoon whereas in the river mouth region it was maximum during the post monsoon season.

Contribution of ammonia-N to the total-N pool of the estuary was <10% during the monsoon and pre monsoon periods. Maximum accumulation of ammonia (>25% of total-N) occured during the post monsoon season. Ammonia showed a significant negative correlation with organic nitrogen during this season ($r = -0.54$ to -0.61, $p < 0.01$) and ammonia was a major component of interstitial water. Thus ammonia distribution in the estuary clearly indicated the process of ammonification in the water column together with the transfer of ammonia from the interstitial water of the bottom sediments. Nitrite concentration was found to be significantly high only during the post monsoon season. The tidal variations during this period showed that nitrite peak was always followed by an ammonia peak and this indicated the process of nitrification.

Heavy rainfall and consequent land drainage brought large amount of nitrate to the estuary during the monsoon season. Nitrate concentration decreased during the post monsoon season and reached minimum values during pre monsoon due to the decrease in land runoff and increased uptake by primary producers. But during this period there was an increase in organic nitrogen concentration. Significant negative correlation ($r = -0.50$ to -0.86, $p < 0.01$) was obtained for nitrate-N with salinity during all seasons.

During the monsoon period, when land drainage and river discharge were maximum, 80-90% of the total-N pool in the estuary was contributed by nitrate alone. On the other hand during the pre monsoon period, when the estuary was marine dominated, 75-85% of the total-N pool was organic nitrogen. Generally an inverse relationship was observed between the inorganic and organic fractions of nitrogen in the estuary. A sharp rise in organic nitrogen accompanied by a depletion of inorganic nitrogen during pre and post monsoon seasons was indicative of phytoplankton productivity and nutrient enrichment due to favourable physico chemical conditions.

The distribution and seasonal variation of phosphorus in the estuary differed from that of nitrogen fractions. Phosphate concentration which was generally low during the pre monsoon period picked up with the advent of monsoon and recorded the highest mean values during the post monsoon season at all sections. Except during certain months inorganic phosphate as well as organic phosphorus was higher at the river mouth than in the upstream sections. Therefore the source of phosphorus in the estuary was mainly from the sea. Regeneration from botom sediments was found to be a major source during the post monsoon season.

The monsoon floods contributed only small amounts of phosphate to the estuary and the decreased concentration observed at sections 1 and 2 could be attributed to adsorption of phosphate to the silty sediment. The interstitial water samples from these sections were found to contain high phosphate concentration. High values of inorganic phosphate observed at the river mouth during July and August could be due to the intrusion of upwelled water.

The nitrogen and phosphorus content of sediments as well as the interstitial water samples showed much higher concentrations at sections 1 and 2 compared to sections 3 and 4. Sediments of sections 1 and 2 are found to contain more clay and silt percentage and so are capable of retaining and recycling nutrients compared to sections 3 and 4 which are composed of sandy bottom. Thus the lower part of the estuary is the more active zone with respect to biogeochemical processes.

Extensive and intensive sampling of current velocities and nutrient concentrations at different water depths were made synoptically for one tidal cycle at 4 sections in the estuary. The computation of instantaneous fluxes of ammonia-N, nitrite-N, nitrate-N and inorganic phosphate was made and presented as mg per m^2 of cross-sectional area.

The results of nutrient flux studies showed that except during the pre monsoon period, there was a net transport of inorganic nutrients into the sea and the rate of transport was mainly controlled by river flow. The net fluxes are found to be lower in the downstream sections than in the upstream sections due to greater biogeochemical and physical processes occurring in the lower part of the estuary. Eventhough there is some utilisation and retention of nutrients within the estuarine system, very large quantities of these, especially the land-derived nutrients are transported to the sea. The quantity of nutrients transported through the Chaliyar river estuary during monsoon (average for June-July, 1991) was estimated to be: Nitrate-N = 13.7 tons per day, Ammonia-N = 1.2 tons per day and Inorganic Phosphate = 0.61 tons per day.

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